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The Mineralogical Society of Japan

Department of Geology and Mineralogy, Faculty of Science, Hokkaido University, Sapporo, Japan

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ON THE ANOMALOUS OPTICAL PROPERTIES OF HEIKOLITE*

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Institute of Mineralogy, Faculty of Science, University of Tokyo

As is widely known certain alkali amphiboles[1)5)10)11)12)13)14)] are anomalous in that they do not show extinction between crossed nicols. An example of such amphiboles is heikolite, a dark green prismatic amphibole. It was found by Y. Kinosaki[9)] in pegmatite in Heikomen,** Korea.

Z. Harada[2)] gave it the formula; $(OH)_2$ (Na, K, Ca, Mn) (Mg, Fe, Fe, Ti, Al)$_5$ (Si, Al)$_8$ O_{22} on the basis of a chemical analysis by S. Komatsu and concluded that the mineral is a variety of alkali amphibole containing approximately 30% glaucophane and 70% riebeckite molecules. The optical properties, too, of heikolite have been studied by several investigators.[9)2)3)]

The most salient characteristics of this mineral is that it does not show on (010) section extinction between crossed nicols with the monochromatic light.

The writer will give below an account of a study of this mineral undertaken to know more about these extraordinary interesting phenomena.

Experimental

As heikolite shows very strong dispersion, it is desirable to employ monochromatic lights of various wave lengths. For this

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* Read at the meeting of the Mineralogical Society of Japan on October 4, 1953.

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purpose, a monochromator was set between the light source and the microscope.

In the spectrum emitted by a helium lamp, the lines at 668, 587, 501, 468 $\mu\mu$ can be used. However, as the intensity of these lines was considerably weak and, moreover, it was not easy to stabilize the source fed by alternating current, an eight-volt lamp fed by a battery was used together with a monochromator to obtain the monochromatic light.

The intensity of transmitted monochromatic light was measured by a photometer[7] which consists of a photomultiplier (RCA 931A) and a galvanometer.

Measurements were made on a relative scale.

Theoretical consideration

Let A be the amplitude of light wave passing through the polarizer whose vibration direction is represented by OP in Fig. 1; upon entering a thin section with vibration direction OX and OZ, it is resolved into two components whose amplitudes are $A\cos\theta$ and $A\sin\theta$ respectively. If these two components pass through the thin section so as to have, at emergence, the phase difference Δ and the absorption ratio e_1, e_2, they will be brought back to the same vibration direction of the analyzer which is represented by OA. The intensity of the resultant of two vibrations which have the amplitude $Ae_a\, e_1 \cos\theta \cos(\chi-\theta)$ and $Ae_a\, e_2 \sin\theta \sin(\chi-\theta)$, when e_a is the reduction ratio of amplitude by absorption or reflection through the analyzer and the other optical parts, is given by

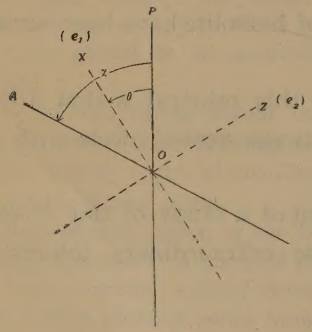

Fig. 1. Diagram showing the vibration direction of light through two nicol prisms and a thin section.

$$I=e^2_a A^2\{e^2_1 \cos^2\theta \cos^2(\chi-\theta)+e^2_2 \sin^2\theta \sin^2(\chi-\theta)$$
$$-2e_1 e_2 \cos\Delta \cos\theta \sin\theta \cos(\chi-\theta) \sin(\chi-\theta)\}$$

The values of e_1, e_2 and Δ are peculiar to a section. Therefore, rotating the section, we obtain a curve of intensity variation with θ for a definite value of χ.

In the case of transparent colorless mineral, we can put $e_1=e_2=1$ in the equation above. Therefore, the theoretical intensity curve is symmetrical with respect to the positions with $\theta=\frac{\chi}{2}\pm n\frac{\pi}{2}$ (maximum positions) and those with $\theta=\frac{\chi}{2}\pm\frac{\pi}{4}\pm n\frac{\pi}{2}$ (minimum positions) where $n=0, 1, 2...$ In addition to this, it can be shown that the difference between the maximum and the minimum for the same value of χ is kept constant $(=e^2_a A^2 \sin^2\frac{\Delta}{2})$ regardless of the value of χ and that the sum of the value of the intensity for $\chi=\frac{\pi}{2}$ and that for $\chi=0$ is $e^2_a A^2$ for the equal value of θ.

In the case of pleochroic mineral, the curve is symmetrical with respect to the positions with $\theta=\frac{\chi}{2}\pm n\frac{\pi}{2}$, but the maximum and the minimum values and their positions vary with the values of e_1, e_2, Δ and χ.

Substituting $-\chi$ for χ, and $\theta-\chi$ for θ in the equation above, we have the same equation; that is, the phase difference between the curve for χ and that for $-\chi$ is χ.

Preliminary experiments with standard minerals

(1) *Topaz.* The (010) section of topaz from the Ebisu Mine,[4] Gifu Prefecture was examined as an example of colorless mineral using the light of $\lambda=668\,\mu\mu$.

For each value of χ, the intensity curve showed the same behaviour at every $\frac{\pi}{2}$ of the angle of rotation and the symmetrical behaviour with respect to the positions of maxima and minima.

The observed intensities which are shown as curves (a), (b) and (c) in Fig. 2 are practically in agreement with those calculated.

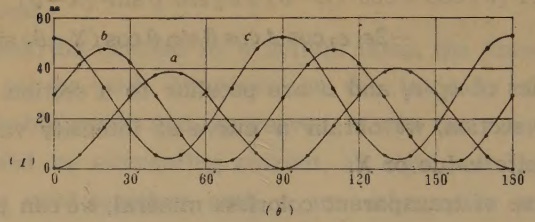

Fig. 2. Intensity variations for the (010) section of topas.
($\lambda=668\,\mu\mu$.) (a) $\chi=90°$ (b) $\chi=40°$ (c) $\chi=0°$

(2) *Aegirine.* The (010) section of aegirine from Kakubuzan,*[9][8] Korea was observed as an example of pleochroic mineral with the light of $\lambda=587\,\mu\mu$ and the intensity was compared with that calculated from the equation.

The values of e_1, e_2 and Δ for this section were determined as follows.

The scale readings on the apparatus with parallel nicols and without section was found to be $e^2_a A^2=275$ mm.
Similarly, for $\chi=0$ and $\theta=0$ we have $e^2_a e^2_1 A^2=8$ mm.,
for $\chi=0$ and $\theta=\frac{\pi}{2}$, $e^2_a e^2_2 A^2=54$ mm.,
for $\chi=\frac{\pi}{2}$ and $\theta=\frac{\pi}{4}$, $\frac{1}{4} e^2_a A^2 (e^2_1+e^2_2-2e_1 e_2 \cos \Delta)=21$ mm.,
and for $\chi=0$ and $\theta=\frac{\pi}{4}$ $\frac{1}{4} e^2_a A^2 (e^2_1+e^2_2+2e_1 e_2 \cos \Delta)=10$ mm..

Assuming that the scale readings on the apparatus is proportional to the intensity to be measured and that $e^2_a A^2=1$, we obtain the values of e_1, e_2 and Δ as follows.

$$e_1=0.170 \quad e_2=0.443 \quad \Delta=121°\ 57'$$

Fig. 3 shows the calculated and the observed values of intensity for $\chi=80°$, where the broken line represents the values calculated using the above values of e_1, e_2 and Δ, and the full line, the corresponding observed values.

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The observed positions of the maxima and the minima determined from the curves for various values of χ are shown as dots in Fig. 4 together with calculated positions which is shown as broken lines. Of the two maxima shown in Fig. 4 and the following figures, Max_1 denotes the one with the larger value and of two minima Min_1 denotes the one with the smaller value.

Each measurement for a definite value of χ was made under the different condition. Therefore, in order to see the variation of the values of maxima and minima, the measurement of the intensity under the same condition was made. The results are shown in Fig. 5 together with

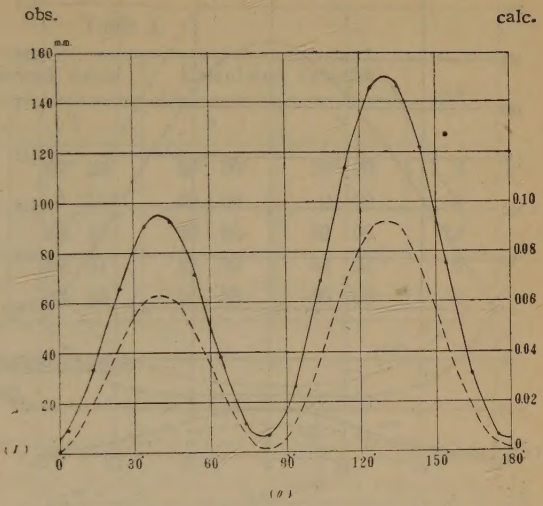

Fig. 3. Intensity variations for the (010) section of aegirine. ($\chi=80°$, $\lambda=587$ μμ.) Full line: observed. Broken line: calculated.

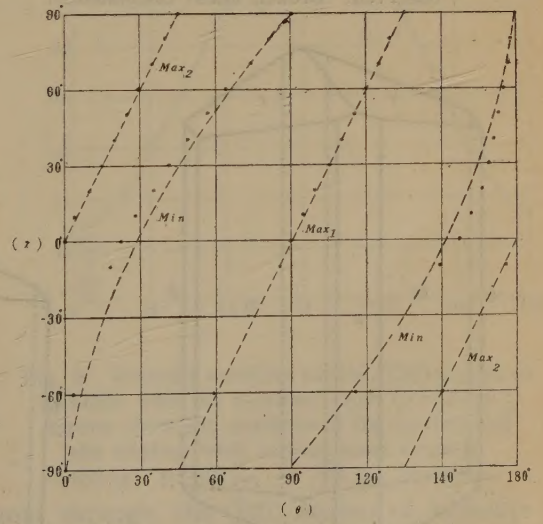

Fig. 4. Positions of maximum and minimum intensity for the (010) section of aegirine. ($\lambda=587$ μμ.) Dots: observed. Broken lines: calculated.

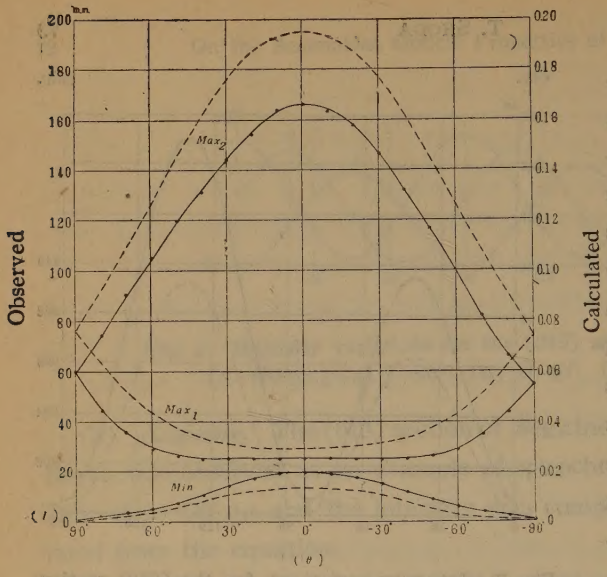

Fig. 5. Variation of the values of maximum and minimum intensity for the (010) section of aegirine. ($\lambda = 587$ μμ.) Dots and full lines: observed. Broken lines: calculated.

the calculated values.

As evident in Figs. 3, 4 and 5, the relative intensities observed are in good accordance with the calculated values.

Measurements on heikolite

The specimen used in this experiment is one from Kansenri,*9) in the crystal form $m(110)$, $r(011)$, $p(\bar{1}01)$, $a(100)$ and $b(010)$ as shown in Figs. 6 and 7. The result of goniometry is shown in Table 1.

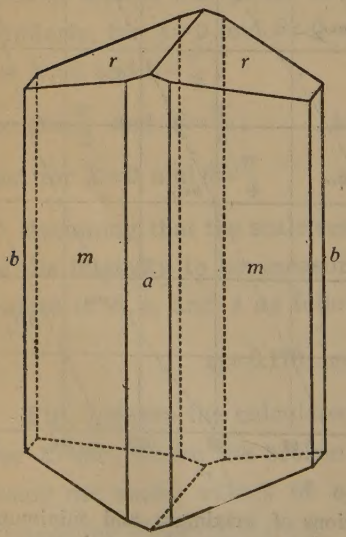

Fig. 6. Crystal form of heikolite from Kansenri having holohedral habit.

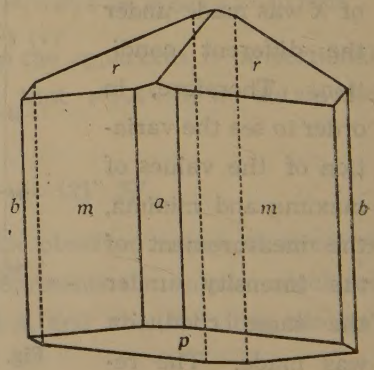

Fig. 7. Crystal form of heikolite from Kansenri having hemimorphic habit.

* Kŏnchh'ŏn-ni, Kŭn-bung-myŏn, Kŭmhwa-gun, Kangwŏn-do, Korea.
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Table 1.

Form	Mean observed value		Calculated value**		n***
	ρ	φ	ρ	φ	
a (100)	00° 00′	90° 24′	90° 00′	90° 00′	3
b (010)	90 02	0 10*	90 00	0 00	5
m (110)	90 00	62 17	90 00	62 05	12
r (011)	22 53	45 51	22 20	44 21	4
p ($\bar{1}$01)	14 18	-90 43	14 58	-90 00	2

* Origin.
** After Goldschmidt's "Winkeltabellen".
*** Number of face measured.

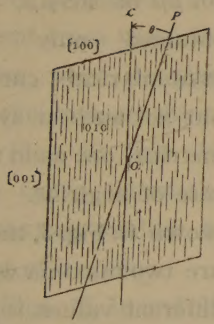

Fig. 8. (010) section of heikolite. OP indicates the vibration direction of polarizer.

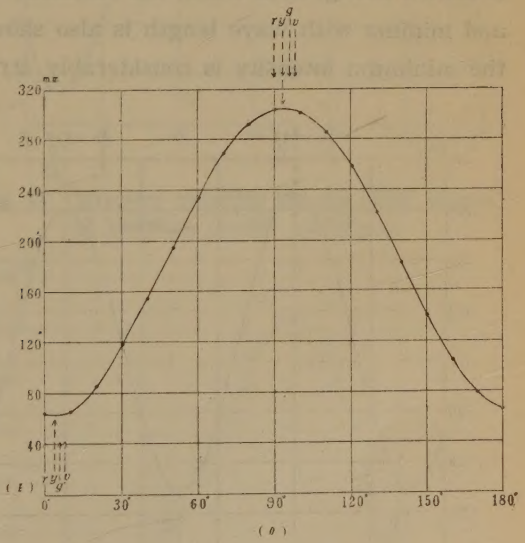

Fig. 9. Intensity variation for the (010) section of heikolite with the polarizer only. ($\lambda = 587\,\mu\mu$.) Arrows show the positions of the maxima and the minima with various wave lengths. r—668 μμ. y—587 μμ. g—501 μμ. v—468 μμ.

The intensity measured through the (010) section of heikolite with the polarizer only, show the maximum value near the position at which the (110) cleavage trace in the section is perpendicular to the vibration direction of the polarizer. ($\theta \fallingdotseq \frac{\pi}{2}$ in Fig. 8) However,

there occurs slight dispersion of the position of the maximum and the minimum intensity. The curve of the intensity variation for 587 $\mu\mu$ is shown in Fig. 9. In this figure, the positions of the maxima and the minima obtained with lights of different wave lengths are also shown.

The curves obtained from the data measured with crossed nicols showed the same behaviour at every $\frac{\pi}{2}$ of the angle of rotation and the symmetrical behaviour with respect to the positions of maxima and minima. However, these positions are shifted considerably with wave length. The curve obtained from the measurement with 587$\mu\mu$ is shown in Fig. 10 in which the variation of the positions of maxima and minima with wave length is also shown. It is to be noted that the minimum intensity is considerably strong.

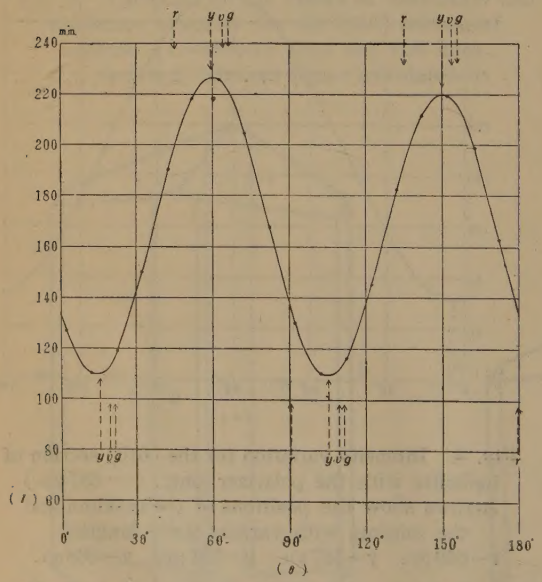

Fig. 10. Intensity variation for the (010) section of heikolite with crossed nicols. (λ=587 $\mu\mu$.) Arrows show the positions of the maxima and the minima with various wave lengths. r—668 $\mu\mu$. y—587 $\mu\mu$. g—501 $\mu\mu$. v—468 $\mu\mu$.

For the measurement with oblique nicols, with 587 $\mu\mu$, 501 $\mu\mu$ or 468 $\mu\mu$, we obtained only an asymmetrical curve, but not such a symmetrical one as in the case of aegirine. As shown in Fig. 3, there are two maxima with different values separated at a distance of $\frac{\pi}{2}$ and two minima with same values symmetrically situated with respect to the positions of the maxima between θ=0 and π. However, in

the case of heikolite, there are two different maxima and two different minima for the larger values of χ, and only one minimum and maximum for the smaller values of χ.

Fig. 11 shows the curve for $\chi=60°$ and $\lambda=501\,\mu\mu$, and Fig. 12 shows that for $\chi=0°$ and $\lambda=501\,\mu\mu$.

For $668\,\mu\mu$, the shape of the intensity curve is slightly different from those for other wave lengths. In this case, as shown in Figs. 13 and 14, the curve shows the behaviour simillar to that of aegirine.

Figs. 15, 16 and 17 show the positions of Max_1, Max_2, Min_1 and Min_2 for different values of χ. From these figures, it will be seen that the angle of θ corresponding to the maximum of the

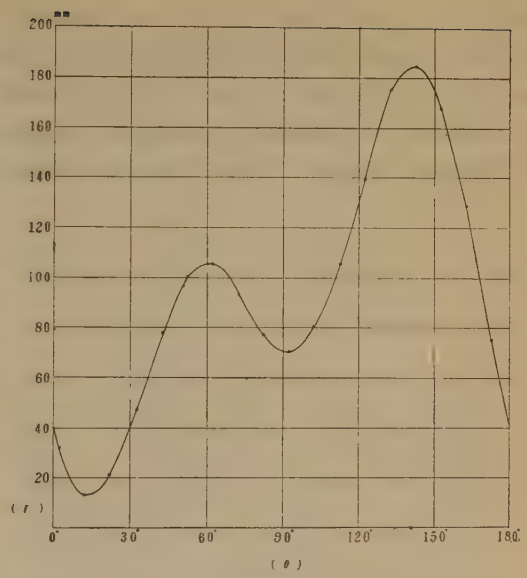

Fig. 11. Intensity variation for the (010) section of heikolite. ($\chi=60°$ $\lambda=501\,\mu\mu$.)

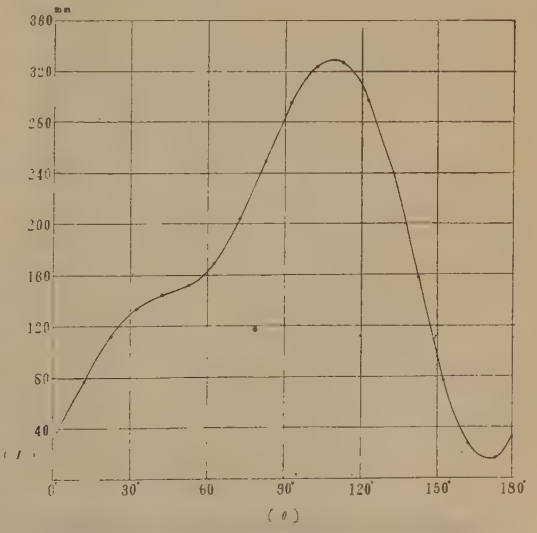

Fig. 12. Intensity variation for the (010) section of heikolite. ($\chi=0°$, $\lambda=501\,\mu\mu$.)

curve for χ is different by χ from that for $-\chi$.

The diagram for the variation of the values of Max_1, Max_2, Min_1 and Min_2 which were measured by the same method as in the case of aegirine are shown in Figs. 18, 19 and 20. In these figures, it will be seen that for 587 $\mu\mu$ the second maximum—Max_2 disappear at the value of $\chi \fallingdotseq 70°$, while that for 468 $\mu\mu$ it can be observed down to $\chi \fallingdotseq 40°$.

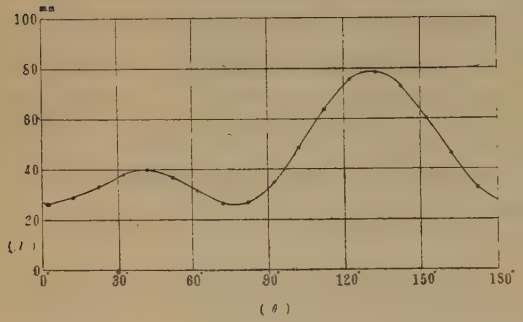

Fig. 13. Intensity variation for the (010) section of heikolite, ($\chi=80°$, $\lambda=668\,\mu\mu$.)

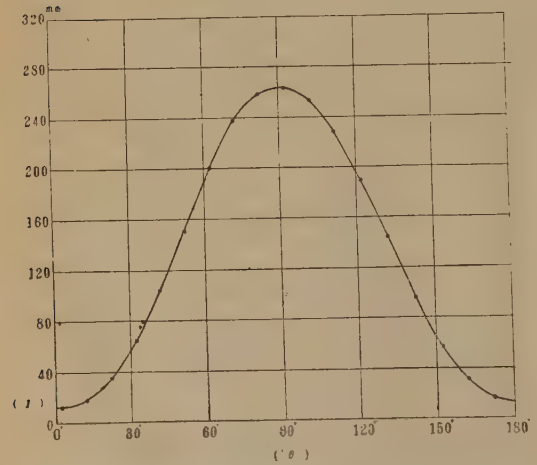

Fig. 14. Intensity variation for the (010) section of heikolite, ($\chi=0°$, $\lambda=668\,\mu\mu$.)

One might consider that the asymmetry of these curves is not due to the optical property of the mineral itself, but due to the deviation of the optical axis of the microscope from the normal of the section. However, this has been shown not to be the case by turning the section inside out and observing it in the direction of $[0\bar{1}0]$ and rotating the stage towards the opposite direction.

The values of the intensity measured for $[0\bar{1}0]$ and $\chi=80°$ are represented by

curve (b) in Fig. 21, in which curve (a) corresponding to those for [010] and $\chi = -80°$ is shown for the sake of comparison. It is readily seen that curve (a) runs parallel with curve (b) and that the positions of the maxima and the minima of curve (a) coincide exactly with those of curve (b). Therefore, there is no appreciable deviation of the direction of the optical axis from that of the normal.

According to the photoelectrical measurement by S. Hori,[3] the values of intensity observed for this mineral were in good agreement with those calculated on the basis of his assumption that this mineral consists of two parts of different orientations. However, the intensity

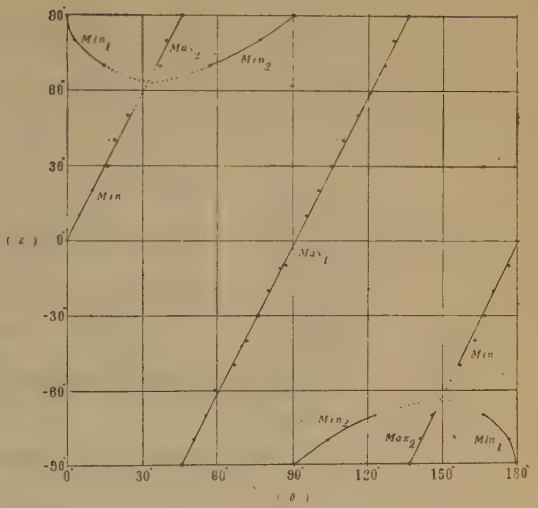

Fig. 15. Positions of maximum and minimum intensity for the (010) section of heikolite. ($\lambda = 668$ μμ.)

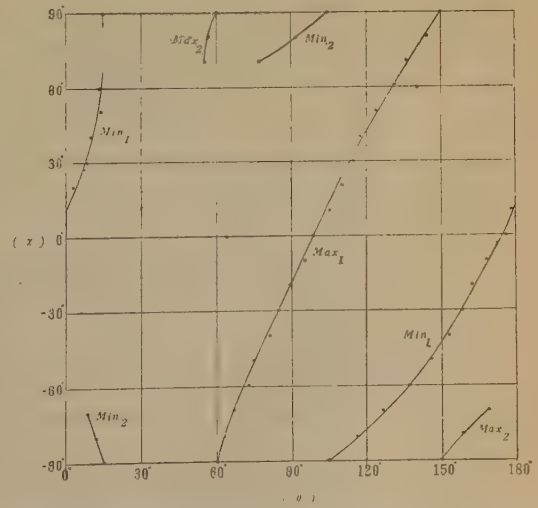

Fig. 16. Positions of maximum and minimum intensity for the (010) section of heikolite. ($\lambda = 587$ μμ.)

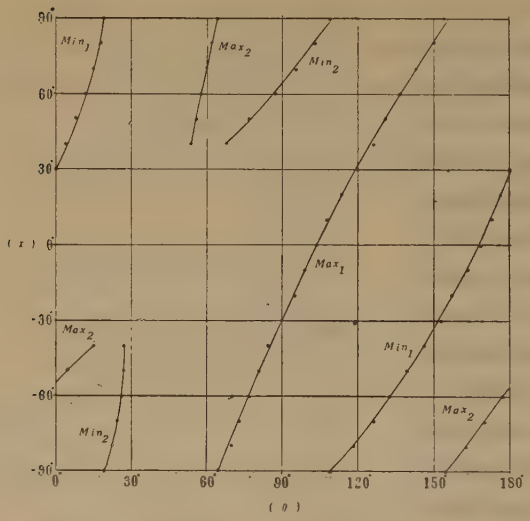

Fig. 17. Positions of maximum and minimum intensity for the (010) section of heikolite. ($\lambda = 468\ \mu\mu$.)

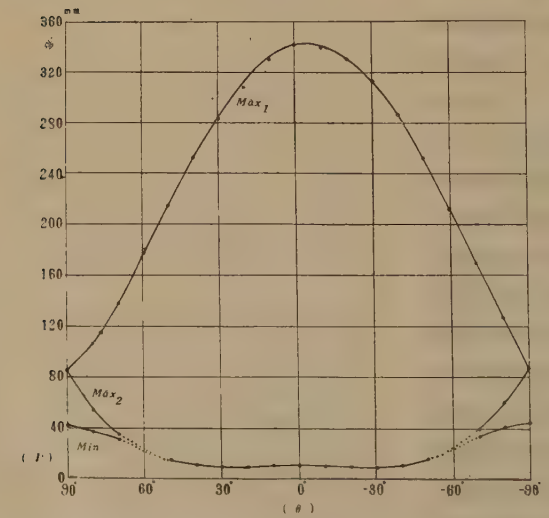

Fig. 18. Variation of the values of maximum and minimum intensity for the (010) section of heikolite. ($\lambda = 668\ \mu\mu$.)

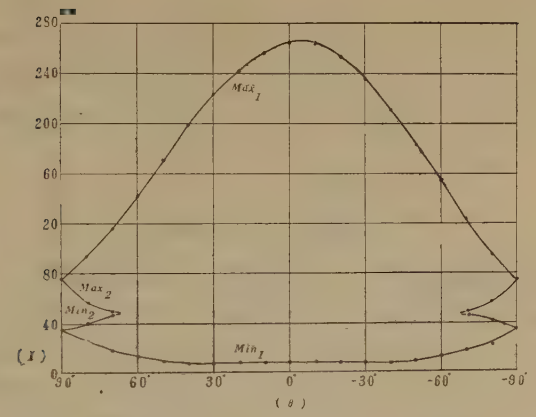

Fig. 19. Variation of the values of maximum and minimum intensity for the (010) section of heikolite. ($\lambda = 587\ \mu\mu$.)

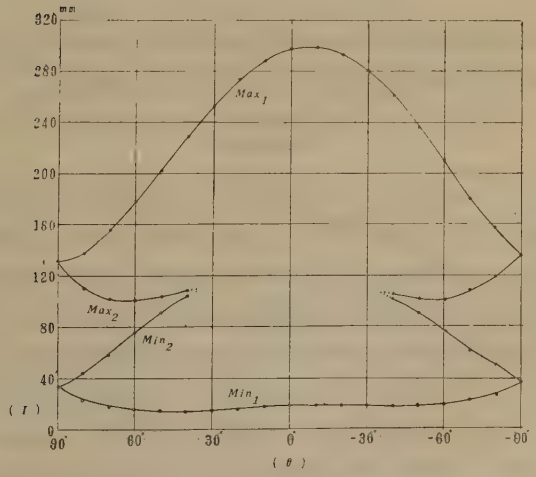

Fig. 20. Variation of the values of maximum and minimum intensity for the (010) section of heikolite. ($\lambda = 468\ \mu\mu$.)

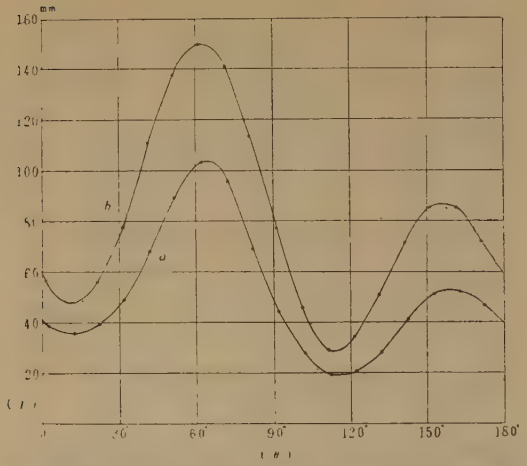

Fig. 21. Intensity variations for the (010) section of heikolite. ($\lambda = 587$ μμ.)
(a) Observed in the direction of [010], for $\chi = -80°$.
(b) Observed in the direction of [0$\bar{1}$0], for $\chi = 80°$.

curves obtained by him is as symmetrical as those for aegirine, and is fairly different from those obtained by the writer.

Summary

The intensity of light transmitted through the (010) section of topaz, aegirine and heikolite was measured by a photomultiplier-galvanometer set with monochromatic lights of various wave lengths.

In both topaz and aegirine, the intensity curve was found to be in agreement with that calculated from the theoretical equation.

For heikolite, the minimum intensity is considerably strong when nicols are crossed, and as χ decreases from 90° to 0°, it gradually decreases until χ takes the value of 40°~50° and then slightly increases with farther decrease of χ.

The intensity curves obtained from the measurement with crossed nicols were found to show the same behaviour at every $\frac{\pi}{2}$ of the

angle of rotation and symmetrical behaviour with respect to the positions of maxima and minima. With oblique nicols, the curves showed asymmetrical behaviour but for the measurement with the light of the wave length 668 $\mu\mu$. However, as in the case of aegirine, the phase difference between the curve for χ and that for $-\chi$ is always χ.

Acknowledgements

The writer wishes to thank Prof. T. Ito, the Institute of Mineralogy, and to Prof. N. Katayama, College of General Education, for their guidance during the present work. He is also indebted to the staff of the Institute of Earth Science and to Mr. K. Nakamura for their assistance in the experiment.

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PAIGEITE (FERROLUDWIGITE) FROM THE KAMAISHI IRON MINE, IWATE PREFECTURE, JAPAN*

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ABSTRACT

Paigeite from Kamaishi, Iwate Prefecture, with a composition near to the Fe end-member of ludwigite group, has been described. The mineral, a product of boron metasomatism related with a granodioritic intrusion, is found as fibrous aggregates associated with magnetite, hedenbergite, andradite, phlogopite, pyrrhotite and chalcopyrite in the iron ores of the skarn type. Its X-ray diffraction pattern is very similar to those of minerals of the ludwigite group. Ore-microscopic observations have been made. Chemical analysis gave the following percentages and formula: SiO_2 1.16, TiO_2 0.11, Fe_2O_3 29.84, FeO 48.72, MnO 0.62, MgO 1.51, CaO 1.60, Na_2O 0.29, B_2O_3 13.24, CO_2 1.14, $H_2O(+)$ 0.70, $H_2O(-)$ 0.52, S 0.09, Total 99.54; $(Fe'', Mg, Mn'')_2Fe'''BO_5$.

Introduction

The minerals of the ludwigite-paigeite series occur usually in dolomite or limestone in granitic regions. They are considered to be the products of boron metasomatism that accompanies a granitic intrusion. Of them magnesium-rich ludwigite is much more abundantly found than iron-rich paigeite, of which the account has been given heretofore only occasionally. Paigeite from Kamaishi, which has an outward likeness to ilvaite, had long been taken for it before we recognized recently as one of the minerals of the ludwigite group.

Mode of occurrence

Paigeite from Kamaishi, Iwate Prefecture, Japan, is found in the

* Read at the joint meeting of the Society of Mining Geologists of Japan and the Mineralogical Society of Japan held in Sendai on October 4, 1953.

contact zone of granodiorite which is intruded into the older porphyrite and Paleozoic fromation consisting mainly of slate and limestone. It is closely intermixed with massive magnetite which, being developed extensively, makes up the main ore body of the Shinyama ore deposit, Kamaishi iron mine. Other minerals associated are hedenbergite, andradite, pyrrhotite, chalcopyrite and calcite. Usually being fibrous aggregates, no outward form has been observed. Fine needles of paigeite are found disseminated in marble that borders the garnet-magnetite skarn mass. The marble is rather poor in magnesia as shown by the result of chemical analysis: SiO_2 9.84%, Al_2O_3 3.77%, Fe_2O_3+FeO 3.91%, MnO 0.14%, MgO 2.94%, CaO 45.14%, Na_2O 0.53%, K_2O 1.34%, Ig. loss 31.82%, Total 99.43%. It is to be noted that the analysed specimen contained a small amount of garnet, phlogopite, apatite, paigeite and tourmaline.

Physical properties

The mineral is dark gray to steel black with silky luster. Opaque. Cleavage is not distinct. Streak is black. The mineral, when free from magnetite and other ingredients, is not magnetic. Specific gravity is 4.53 (measured by a pycnometer at the room temperature). Hardness is about 5.

Microscopic observations

Although usually opaque, the extremely fine needles embedded in marble show pleochroism under the microscope: Z'//elongation, brown; X' $\perp$ elongation, deep green (Plate I, Fig. 1). Absorption $Z' > X'$. Extinction straight. Polished surfaces are usually smooth under the ore-microscope. Parting is observed rarely. Intermediate hardness. Colour varies from brownish gray to dark bluish gray in air as well as in oil. Internal reflexion is occasionally observed with the oil-immersion lens. Reflexion-pleochroism is very distinct: // elongation, grayish brown; $\perp$ elongation, bluish gray. Between

the crossed nicols anisotropism is very strong, too (Plate I, Fig. 2). Intensive manifold polarization-colour is observed: reddish brown to pale grayish blue. Four extinctions per revolution. Etch reactions after Short's method negative. Paigeite with these characteristics is very similar to ludwigite and has some in common with ilvaite.

Chemical composition

Fibrous aggregates apparently free from sulphides and other impurities were treated with warm concentrated HCl for a short time and analyzed by the usual methods. The result given in Table 1, has revealed that the mineral has the composition, 4 (Fe, Mg, Mn) $O \cdot Fe_2O_3 \cdot B_2O_3$ or $(Fe'', Mg, Mn'')_2 Fe'''BO_5$ with the ratio $Fe'' : Mg : Mn'' = 0.94 : 0.05 : 0.01$. The mineral, containing 94% $Fe''_2 Fe'''BO_5$

Table 1. Chemical analysis of paigeite from Kamaishi

	1	2	3	4	5
SiO_2	1.16%	0.0193			
TiO_2	0.11	0.0014			
Al_2O_3	—	—			
Fe_2O_3	29.84	0.1869	0.1869	1.0	30.90%
FeO	48.72	0.6782			55.62
MnO	0.62	0.0087	0.7244	3.8	
MgO	1.51	0.0375			
CaO	1.60	0.0285			
Na_2O	0.29	0.0047			
B_2O_3	13.24	0.1901	0.1901	1.0	13.48
CO_2	1.14	0.0269			
H_2O (+)	0.70	0.0389			
H_2O (−)	0.52	0.0289			
S	0.09				
Total	99.54%				

1. Paigeite from Kamaishi. Analyst J. Ito.
2, 3, 4. Molecular ratios.
5. Theoretical composition of paigeite: $Fe''_2 Fe''' BO_5$.

against 5% $Mg_2Fe'''BO_5$ molecules, is one of the nearest to the Fe-rich end member of the ludwigite-paigeite series so far known.

X-ray examination

The X-ray powder spectrograms of paigeite taken by means of a Philips Norelco Spectrometer have been compared with those of ludwigites from Hol Kol, North Korea and other localities with a close agreement between them as shown in Table 2.

Table 2. Ludwigite and paigeite: X-ray diffraction pattern (Fe Kα radiation)

	1		2		3		4		5	
(h k l)	d	I	d	I	d	I	d	I	d	I
(110)	7.42	1	7.42	1	7.42	1	7.52	½	7.47	½
(020)	6.19	1½	6.19	1	6.16	1	6.16	1	6.19	½
(120)	5.134	10	5.146	9	5.146	9	5.17	5½	5.146	5
(230)	3.045	1	3.037	1	3.013	1½	3.029	1½	3.037	2½
(240)	2.564	10	2.569	10	2.569	10	2.575	10	2.572	10
	2.542	2	2.537	1	2.531	1	2.542	½	2.531	1
(250)	2.175	2	2.175	4	2.175	3	2.18	2	2.182	2
(321)	2.043	1	2.040	½	2.057	2	2.07	1½	2.067	1
(160)	2.008	1	2.006	2	2.004	1	2.008	1	2.004	1
	1.926	½	—		1.926	2	1.937	1	1.937	1
	1.774	1	1.774	½	1.776	1½	—		—	
	n. d.		n. d.		n. d.		1.539	1	1.539	1½
	n. d.		n. d.		n. d.		1.399	1	1.397	2½

1. Ludwigite from Hol Kol, North Korea.
2. Ludwigite from Kilbride, Skye.
3. Paigeite (vonsenite) from Riverside, California.

} $2\theta = 5° \sim 70°$

4. Paigeite (a) (analysed specimen) from Kamaishi, Japan.
5. Paigeite (b) from Kamaishi (450 m. level), Japan.

} $2\theta = 5° \sim 90°$

Acknowledgements

We wish to thank to Prof. T. Ito for critically reading the manuscript and valuable suggestions and also to Mr. S. Imai, Superintendent of the Kamaishi mine, and Mr. N. Wada, chief geologist of this mine for their kind aids in our field surveying. We are also much indebted to Prof. C. E. Tilley of Cambridge University, Dr. W. F. Foshag, National Museum, Washington, D. C., Prof. T. Sakamoto of the University of Tokyo, and Mr. H. Ōmachi of Hokkaido University for samples of ludwigite and vonsenite. Further acknowledgements are made to Messrs. J. Ossaka and S. Takasu, for their kind aids in X-ray studies. This investigation was aided by a grant from the Scientific Research Fund of the Department of Education in 1953.

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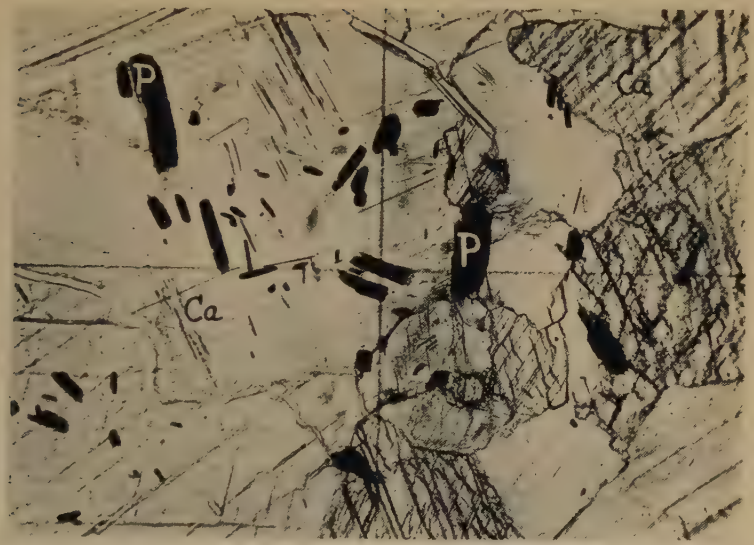

Fig. 1. Photomicrograph of a thin section of paigeite-bearing marble. Fine needles of paigeite (P) are embedded in granular aggregate of calcite (Ca). ×90

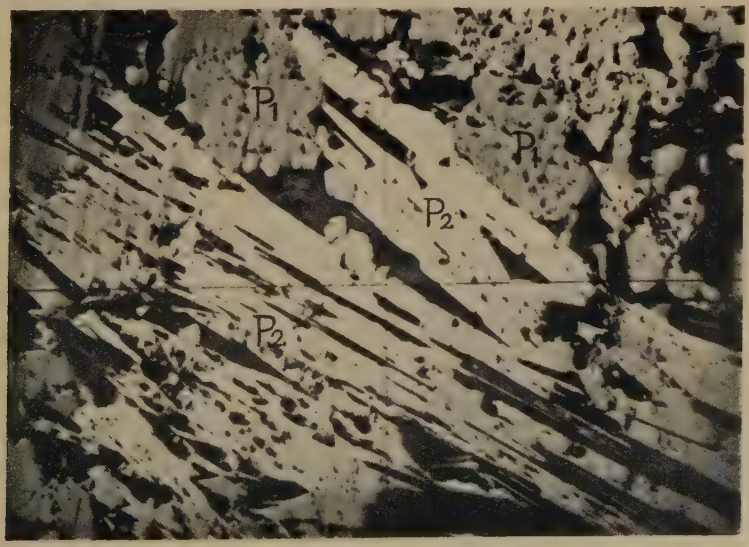

Fig. 2. Photomicrograph of a polished section of paigeite-bearing iron ore. P_1: basal section of paigeite, P_2: prismatic section of paigeite. Fibrous aggregates of paigeite showing its strong anisotropism in diagonal position. ×120

MINERALOGICAL JOURNAL, VOL. 1, NO. 2, PP. 89-96, MAY, 1954

ON CLINOCLASITE FROM KITABIRA, YAMAGUCHI PREFECTURE, JAPAN*

(Studies on the Arsenate Minerals from Japan, Rept. 6)

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ABSTRACT

Clinoclasite, a basic arsenate of copper, from the Kitabira mine, Yamaguchi Prefecture has been described. It is found usually as massive aggregates of small flakes with limonite or iron-rich clay. The crystal is platy parallel to (001), and has monoclinic symmetry. The cell dimensions are $a_o = 12.48$Å, $b_o = 6.48$Å, $c_o = 7.27$Å and $\beta = 99°02'$ (morphologically). Forms: $c(001)$, $a(100)$, $m(110)$, $n(810)$, $v(\bar{1}21)$ and $s(\bar{5}52)$. Colour: greenish blue or deep blue. Streak: bluish green. Translucent. Hardness 2.5~3. Cleavage (001) perfect. Sp. gravity 4.33 (9°C). Opt. properties: $\alpha = 1.739$, $\beta = 1.87$, $\gamma \fallingdotseq 1.9$, $2V \fallingdotseq (-)$ 50°: $v > r$ strong; $a \perp Z$ ($c \wedge X \fallingdotseq 10°$); Pleochroic. Chemical analysis follows, As_2O_5 29.66, Al_2O_3 0.63, Fe_2O_3 0.32, CaO 0.05, CuO 62.42, $H_2O(+)$ 7.55, $H_2O(-)$ 0.36, total 100.99%. The X-ray powder diagram of this specimen agrees well with the data given by Palache and Berry.

Introduction

Four hydrated or basic arsenate minerals have been reported from Kitabira mine, namely scorodite ($FeAsO_4 \cdot 2H_2O$),[4] olivenite ($Cu_2AsO_4(OH)$)[2][3][5][5][7][11], cuproadamite ($(Cu, Zn)_2AsO_4(OH)$),[6] and conichalcite ($(Ca, Cu)_2(AsO_4)(OH)$)[8]. In addition to these minerals greenish blue massive clinoclasite, a rare mineral species of basic arsenate of copper, has been found recently from the same locality. The minerals mentioned above are considered to be the origin of arsenic in the limonite ore of the Kitabira mine.

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* This investigation was carried out at the Institute of Mineralogy, University of Tokyo. A preliminary report of this work was read at the meeting of the Geological Society of Japan in March 1950.

In 1947 the writer was offered a specimen of clinoclasite from the Kitabira mine by Mr. K. Sakurai, and in the summer of the same year we personally collected the mineral from the mine. The next year we found clinoclasite in the late Doctor T. Katō's mineral collection in Kyushu Technical College, labelled as occurred in the Naganobori mine, Yamaguchi Prefecture. It may have been collected from the Kitabira ore deposit, Naganobori mine* between 1905 and 1915.

In February 1950 a chemical investigation of the mineral was published by K. Sakurai and his coworkers[10], and in March 1950 the writer reported a mineralogical study of the mineral. The detail of the study are given below.

Occurrence

The Kitabira mine** is in Oota-machi, Miné-gun, Yamaguchi Prefecture*** and is situated at about 15 kilometers northwest of Yamaguchi City, Yamaguchi Prefecture. The Kitabira ore deposit of this mine, the locality of this clinoclasite, is a contact-metasomatic type formed in palaeozoic limestone intruded by granitic rocks. The ore body takes an inclined cylindrical shape. The primary mineral zone consists of sulphide minerals such as arsenopyrite, pyrite, pyrrhotite, chalcopyrite etc. and the oxidized zone is altered to limonite with other secondary products of sulphide mineral.

The occurrence of the clinoclasite in this deposit is of two types: one is found as a cementing matter of limonite fragments; the other is as massive aggregate including iron-rich clay. It is associated with none of other arsenate minerals.

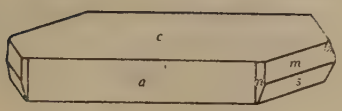
Crystal morphology

Clinolcasite from the Kitabira mine has a greenish blue colour and has massive or botryoidal appearance. It is composed of small

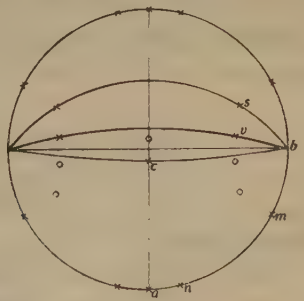
* Now this ore deposit is called the Kitabira ore deposit, Kitabira mine. 長登鉱山北平鉱床, ** 喜多平鉱山, *** 山口県美禰郡大田町

foliated crystals arranged in random or radial orientations. Each individual crystal is about 1 mm. long and about 0.2 mm. thick. Only one crystal was measured on the V. Goldschmidt's two circle goniometer.

The crystal has six forms, of which two forms, $c(001)$ and $a(100)$, show good reflection and the other forms, $m(110)$, $n(810)$, $v(\bar{1}21)$ and $s(\bar{5}52)$, show poor reflection. Of them two forms, $n(810)$ and $v(\bar{1}21)$, are the new forms. The angle between $c(001)$ and $a(100)$ was accurately measured as 80°58′. It shows that the value of angle β is 99°02′. The results is in fairly well agreement with that which has been obtained by Palache and Berry[9]. Measured angles are listed in Table 1 compared with the calculated values that were determined on the basis of the values $a:b:c=1.9109:1:1.1223$, $\beta=99°22'$[9]. Crystals are platy in (001) and elongated along [010] with large developments of (001) and (100), as shown in Fig. 1. A stereographic projection of the crystal is shown in Fig. 2.



$c(001)$, $a(100)$, $m(110)$, $n(810)$. $v(\bar{1}21)$, $s(\bar{5}52)$.
Fig. 1. Clinoclasite crystal from Kitabira.



$c(001)$, $a(100)$, $m(110)$, $n(810)$, $v(\bar{1}21)$, $s(\bar{5}52)$.
Fig. 2. Stereographic projection of clinoclasite.

Physical and optical properties

The specimen of this locality has following characters: Colour: greenish blue or dark blue. Translucent. Luster: vitreous, pearly

Table 1. Two-circle angles of clinoclasite.

Forms	Measured value		Calculated value*	
	ρ	φ	ρ	φ
m (110)	89°	28°	90°00′	27°56′1/2
n (810)	90	77	„	76 44 1/2
a (100)	90°00′	90°00′	„	90 00
c (001)	9 02	„	9 22	„
v ($\bar{1}21$)	64°2/3	- 8°	66 22 1/2	-10 54
s ($\bar{5}52$)	73	-25 2/3	72 08	-25 15

* Calculated on the basis of the values a : b : c = 1.9109 : 1 : 1.1223, β = 99°22′[9].

on cleavage. Cleavage: (001) perfect. Hardness: 2.5~3. Brittle. Streak: bluish green. Specific gravity is measured as 4.33 at 9°C by means of a picnometer.

The indices of refraction were measured by the dispersion method. Because of the high value of the indices of refraction β and γ could not be determined as good as α. The optical angle, dispersion, pleochroism and optical orientations are given in Table 2 compared with those of clinoclasite from Majuba Hill and from Tintic, Utah.[9]

Table 2. Optical properties of clinoclasite.

	Kitabira	Majuba Hill & Tintic, Utah*
Refractive indices		
α	1.739	1.756[9]
β	1.87	1.874
γ	1.9	1.896
2V	Nearly (−) 50°	(−)50°[9]
Dispersion	v > r very strong	v > r very strong
Pleochroism		
X	Pale blue or pale green	Pale blue-green
Y	Bluish green	Light blue-green
Z	Brownish or yellowish	Benzol green
Orientation	c∧x nearly 10°	
	Y//b	Y//b
	Z //. a	Z //. a

* After the Dana's System of Mineralogy, vol II, 7th Ed.[1].

Chemical composition

The specimen was first tested by means of chemical microscopy, determining copper and arsenic. Material for chemical analysis was obtained by a handsorting method from the crushed sample under the low-power microscope. The obtained sample contained no appreciable amount of impurity when examined under the petrographic microscope with high-power objective. A sample was used for the determinations of $H_2O(-)$, As_2O_5, Al_2O_3, Fe_2O_3, CuO and CaO, and another, for the $H_2O(+)$ by the Penfield method.

The results are given in Table 3 compared with the theoretical composition of clinoclasite. After reducing Al_2O_3 and Fe_2O_3 as the not-ascertained impurities, the atomic ratio is calculated from the weight percentage. This ratio yields the formula $Cu_{3.0}(OH)_{3.0}(AsO_4)_{1.0}+1/10H_2O$. The formula agrees closely with that of clinoclasite, namely $Cu_3(OH)_3(AsO_4)$. The analysis shows a small amount of water in excess of the calculated value. Part of the excess may be the composition of the clinoclasite as is usually observed in botryoidal minerals and the remainder may be the component of impurities.

Table 3. Chemical analysis and atomic composition of clinoclasite.

	$Cu_3(OH)_3(AsO_4)$	Kitabira		
	Wt. %	Wt. %	Mol. prop.	Atom. rat.
As_2O_5	30.19%	29.66%	.129	As 1.95
Al_2O_3	—	0.63	—	
Fe_2O_3	—	0.32	—	
CaO	—	0.05	—	
CuO	62.71	62.42	.785	Cu 5.95
$H_2O(+)$	7.10	7.55	.419	(OH) 6.00
$H_2O(-)$		0.36	.020	H_2O 0.18
Total	100.00	100.99		

(Analysed by H. Minato, 1948)

X-ray experiment

The X-ray powder pattern of the clinoclasite from Kitabira by means of Phillip's X-ray spectrometer was compared with that of the specimens from Tintic District, Utah and other localities[9], and a close agreement was found between them. The observed intensities and measured spacings are listed in Table 4 compared with the indices and calculated values[9].

The spacings of the clinoclasite from this locality are calibrated by means of the quartz powder patterns. Furthermore, the values of a_0, b_0 and c_0 were calculated from the spacings of (200), (020), (040), (002) and (003) and angle β (determined morphologically). The results are listed in Table 5 compared with the cell dimensions of clinoclasite of other localities[9]. The values of clinoclasite from Kitabira are somewhat larger than that of other localities.

Table 4. X-ray powder pattern of clinoclasite.

Tintic & other localities*			Kitabira			Theoretical value*	
I (Cu)	θ(CuKα)	d (meas.)	I(Cu)	θ (CuKα)	d (meas.)	(hkl)	d (calc.)
			4	5.5°	8.04 Å		
3	6.0°	7.55kX	22	6.13	7.213	(001)	7.13kX
3	7.0	6.3	13	7.18	6.163	(200)	6.10
1	9.4	4.7	6	9.48	4.677	($\bar{1}11$)	4.63
6	10.4	4.3	13	10.21	4.345	(201) (111)	4.30 4.29
1/2	11.1	3.99	8	11.16	4.013	($\bar{2}11$)	3.98
10	12.5	3.55	5	11.98	3.712	(211)	3.57
			100	12.40	3.587	(002)	3.56
			6	12.83	3.470		
			6	13.28	3.351		
			5	13.77	3.236	(020)	3.24
8	14.2	3.13	24	14.22	3.139	($\bar{1}12$) (012) (120)	3.13 3.12 3.12
			14	14.59	3.060		
3	14.9	2.99	13	14.88	3.000	($\bar{4}01$)	2.99
			7	15.01	2.975	($\bar{2}12$)	2.96
			7	15.18	2.942		
4	15.5	2.88	10	15.34	2.913	($\bar{1}21$)	2.90
			5	15.64	2.857	(202)	2.88
3	15.7	2.84	7	15.85	2.821	(220) (121)	2.85 2.81
1	16.1	2.77	6	16.20	2.761	(410)	2.76

			5	16.38	2.732		
3	16.8	2.66	5	16.55	2.704	(3̄12)	2.67
			9	16.85	2.657	(401)	2.65
4	17.7	2.53	8	17.65	2.540	(4̄02)	2.53
						(320)	2.53
4	18.0	2.49	9	18.18	2.469	(3̄21)	2.46
						(411)	2.45
						(1̄22)	2.40
3	18.8	2.38	13	18.80	2.390	(022)	2.39
						(003)	2.38
			5	19.05	2.361		
			6	19.32	2.328	(312)	2.32
						(2̄22)	2.31
5	19.5	2.30	8	19.47	2.311	(321)	2.31
						(122)	2.30
4	20.1	2.24	6	19.87	2.267	(1̄13)	2.26
			14	20.10	2.242	(013)	2.23
						(402)	2.148
3	21.0	2.14	7	21.02	2.147	(222)	2.147
						(113)	2.136
4	21.5	2.10	8	21.43	2.110	(203)	2.100
						(3̄13)	2.094
						(031)	2.058
						(421)	2.047
5	22.0	2.05	9	22.04	2.053	(1̄31)	2.046
						(6̄01)	2.045
						(4̄03)	2.045
						(412)	2.038
1/2	23.0	1.967				(2̄31)	1.979
						(322)	1.968
1	23.7	1.912	5	23.73	1.914	(6̄02)	1.906
						(132)	1.844
2	24.7	1.839	5	24.65	1.847	(032)	1.841
						(313)	1.839
						(5̄12)	1.799
2	25.4	1.792	6	25.23	1.807	(2̄04)	1.792
						(422)	1.787
3	26.6	1.717	6	26.45	1.729	(014)	1.718
						(6̄03)	1.688
			6	27.15	1.6879	(710)	1.681
2	27.1	1.687	5	27.38	1.6750	(3̄14)	1.681
						(413)	1.680
			5	27.68	1.6584		
						(6̄22)	1.641
2	27.9	1.643	6	27.85	1.6488	(204)	1.640
						(4̄31)	1.639
						(040)	1.612
2	28.5	1.611	5	28.33	1.6234	(4̄14)	1.610
			5	29.10	1.5838		
			5	29.45	1.5666		
			6	29.80	1.5499	(8̄01)	1.543
4	29.9	1.542	5	30.03	1.5394	(3̄33)	1.543
3	31.0	1.492	5	31.03	1.4944		
1	31.6	1.467					
3	32.6	1.427	7	32.45	1.4355		
3	32.9	1.415	5	32.90	1.4180		
1	33.6	1.389	5	33.25	1.4048		

* After the results which was given by Palache and Berry[9].

Table 5. Cell dimensions of clinoclasite.

	Tintic, Utah[9]	Nevada[9]	Cornwall[9]	Kitabira
a_0	12.37kX	12.33Å	12.36kX	12.48Å
b_0	6.45	6.42	6.45	6.48
c_0	7.24	7.21	7.23	7.27
β	99°25′	99°22′	99°30′	99°02′*

* Determined morphologically.

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The writer wishes to express his sincere thanks to Professor Teiichi Ito of the Mineralogical Institute, University of Tokyo, for his kindly helps during the present investigation. Further acknowledgements are due to Mr. Shinichiro Takasu of the same institute for his assistances in X-ray experiments. He is indebted greatly to Professor Nobuo Katayama of College of General Education, University of Tokyo, for his critical reading of the manuscript and useful suggestions. The writer is grateful to Mr. Kin-ichi Sakurai and Mr. Akira Hayashi to whom he owed some of the specimens used in the study.

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ON THE THERMO-ELECTRIC POTENTIAL OF PYRITE FROM THE TUTIYA ISIZAKI MINE, HOKKAIDO, JAPAN.*

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ABSTRACT

The thermo-electric potentials of the pyrite from the Tutiya Isizaki mine, Hokkaidô, Japan were determined. The data obtained showed considerable variations. X-ray diffraction, microscopic, chemical and spectrographic studies were performed to ascertain the controling factor of the variation.

The results indicated that the effect of structural irregularities should be noted in particular among several factors causing the variation of thermo-electric properties of pyrite.

Introduction

Many experimental works have been carried out on the thermo-electric properties of pyrite. It is known that the thermo-electric properties of pyrite vary from specimen to specimen in magnitude as well as in sign. The variations may be attributed to several factors of which occurrence, crystal habit and surface state, disturbances of lattice and impurities may be mentioned here.

It seems highly probable that there exists some relation between the thermo-electric properties and structural irregularity. In order to ascertain which of this and other factors count really the authors have performed a series of experiments. As the material for the experiments pyrite crystals from the Tutiya Isizaki mine, Hokkaidô have been chosen. They are well-formed cube and are apparently homogeneous.

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* Read at the meeting of the Mineralogical Society of Japan on October 4, 1953.

Geological occurrence and crystal habit

The Tutiya Isizaki mine, in which suitable specimens of pyrite are found is located in Isizaki, Zenikamézawa village, Kaméda County, Osima Province, Hokkaidô*, 12 kilometers east of Hakodaté City.

The deposit lies in folded sedimentary rocks of Palaeozoic age consisting of phyllite and sandstone. Pyrite quartz veins make up the deposit. Besides pyrite and quartz we find chalcopyrite, galena and sphalerite in small quantity.

One of the veins (called No. 5) produces well-formed cube crystals of pyrite. The vein varies considerably in width attaining to eight meters. Most of the pyrite crystals found are usually less than two centimeters but sometimes over eight centimeters in dimensions. Crystals of the pyritohedral type are also observed.

In another vein (called No. 9) rather more copper rich, occur

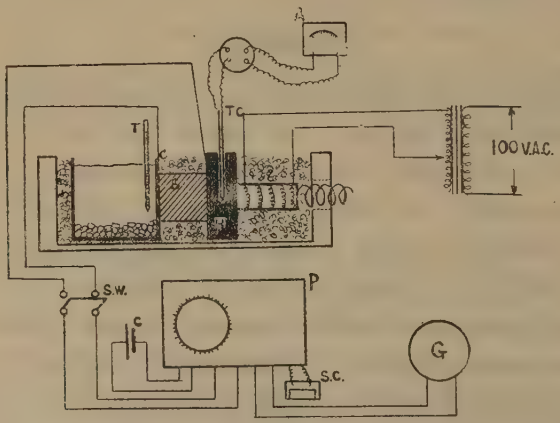

Fig. 1. Apparatus for measuring thermo-electric potential.
A: Ampere meter P: Potentiometer C: Cell
S.C.: Standard Cell G: Galvanometer
S.W.: Switch H: Hot junction (copper plate)
C: Cold junction (copper box) S: Specimen
T.C.: Thermo-couple T.: Thermometer

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pyrite crystals also of the cubic type as well as of the type intermediate between the cubic and the pyritohedral type.

The specimens from No. 5 vein were mainly used together with some from No. 9 vein.

Measurement of thermo-electric potential

The measurements of thermo-electric potential were carried out using the method similar to that of K. Hayasé. (Fig. 1.)

To minimize the surface effects homogeneous crystals with a smooth and bright surface were selected. The selected crystals were treated with alcohol and 0.01 N hydrochloric acid. The specimens were further examined under the ore-microscope and those free from inclusions were selected for experiments.

The apparatus is designed so that one side of the fixed copper box is used as the cold electrode, while a thick copper plate, about eight millimeters thick, serves as the hot electrode made movable by a spiral spring. The hot junction is heated with an electric coil and the cold one cooled with ice and water. A copper-constantan thermocouple is inserted into a deep hole in the copper plate of the hot electrode for the precise measurement of temperature. Copper was used as the reference metal.

The specimens were measured at 150°, 120°, 100°, 60° and 30°C respectively. Several measurements were made on each specimen at each temperature and the values of potential were read on the potentiometer and the reading were averaged.* Calibration of the potentiometer was performed at every measurement, since it was very sensitive to temperature variation.

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* For example the results of measurements of thermo-electric potential of the specimen 5a at 30°C are cited as follows:

[100]	−[100]	[010]	−[010]	[001]	−[001]	Mean value $E_{30°}$
1.61	1.60	1.58	1.58	1.56	1.58	1.59
1.58	1.57	1.62	1.62	1.59	1.58	
1.59	1.59	1.61	1.61	1.57	1.57	
1.59	1.58	1.59	1.60	1.62	1.61	

Table 1. The results of the measurement of thermo-electric potential of pyrite from the Tutiya Isizaki mine.

No. of specimen	Thermo-electric potential of pyrite				
	$E_{30°}$	$E_{60°}$	$E_{100°}$	$E_{120°}$	$E_{150°}$
1a	0.27mV	0.50mV	1.35mV	2.63mV	6.21mV
1b	0.13	0.26	2.13	1.92	1.85
2a	−1.76	0.42	2.26	4.83	8.69
2b	2.59	4.21	4.87	5.38	6.30
2c	1.25	1.36	6.29	9.42	12.37
3a	0.93	2.27	8.66	11.79	12.37
4a	0.26	1.98	6.75	10.11	10.23
4b	−0.02	−1.26	−2.57	−3.67	−4.95
4c	3.27	3.15	4.51	5.79	9.87
5a	1.59	3.03	3.87	6.22	13.26
5b	−1.11	−1.24	−2.38	−2.99	4.29
6a	−0.03	−0.77	−0.92	−1.13	−1.01
6b	−1.51	−1.53	−1.97	−2.11	−3.21
6c	−0.33	−0.90	−2.78	−3.84	−6.07
7a	−0.32	−0.97	−1.91	−3.66	−5.03
7b	−2.08	−3.69	−5.51	−7.25	−11.39
7c	−1.37	−1.81	−3.92	−6.34	−8.22
8a	1.10	1.29	5.38	9.21	13.63
8b	−2.36	−2.23	−4.41	−4.52	−2.93
8c	0.35	0.26	0.21	0.52	0.83
9a	0.63	3.77	7.38	10.59	12.53
9b	0.31	1.68	4.63	6.34	7.41
9c	0.07	1.50	6.38	8.21	10.91
10a	0.30	1.37	3.40	4.32	8.13
10b	1.55	0.96	2.67	3.52	8.91
10c	0.05	0.31	1.29	1.56	2.08
11a	0.09	0.07	0.38	0.52	0.82
11b	0.52	0.84	1.88	2.55	3.40
11c	1.18	1.27	1.99	3.82	5.45
12a	1.17	1.20	3.61	8.55	17.36
12b	2.29	3.70	3.90	4.21	4.64
13a	−0.02	−1.21	−1.35	−2.56	−3.26
13b	1.17	1.79	2.67	3.55	4.71

Table 1.—*Continued*

13c	1.53	2.30	4.34	5.62	8.34
14a	−0.27	−0.46	0.22	0.66	2.53
14b	2.59	3.51	8.82	13.26	17.80
15a	1.94	3.90	7.29	12.77	12.05
16a	2.56	1.53	4.41	7.32	10.80
16b	0.08	0	0	−0.09	−0.03
17a	2.53	1.09	3.26	5.65	18.78
17b	1.39	2.10	4.33	4.26	6.24
17c	0.52	1.22	7.31	11.59	15.70
18a	−2.42	−1.13	4.31	7.82	10.60
18b	0.29	1.68	3.87	5.50	7.09
18c	1.35	3.21	8.63	13.66	19.82
19a	1.33	2.55	3.82	4.56	6.20
19b	1.12	1.37	3.57	4.26	6.78
19c	1.54	2.40	5.66	8.26	9.91
20a	0.52	1.45	3.31	5.39	7.41
20b	0.53	0.14	0.80	1.56	0.97
20c	1.12	1.15	2.91	3.03	5.22
* 21a	0.83	3.61	−3.52	−7.63	−12.32
* 21b	−1.13	−2.65	−6.38	−8.25	−9.90
* 21c	−3.29	−1.14	−1.12	−1.08	−1.36
* 21d	−0.59	−1.11	−3.36	−5.32	−6.18
* 21e	3.93	2.67	0.10	−5.17	−6.28
* 21f	−0.03	−1.31	−2.75	−3.96	−6.07

* The specimen from No. 9 vein.

The sign of thermo-electric potential is given as usual. Potential of pyrite is taken positive against the reference material (copper) if the thermal current flows in the same direction as the electric current when the circuit is closed, and negative, if the thermal current is reversed.

The results of measurements are given in Table 1. Fig. 2 shows some of them graphically.

Among the specimens from No. 5 vein those which are intimately associated with copper ores show negative thermo-electric potentials,

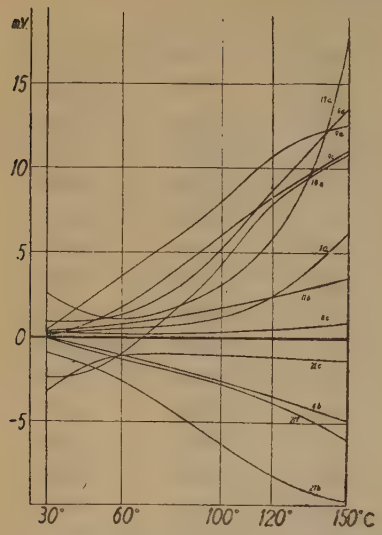

Fig. 2. Thermo-electric potentials of some pyrites from the Tutiya Isizaki mine, versus copper.

while all the specimens from No. 9 vein, a copper pyrite quartz vein, show negative values.

When we set the specimen in the opposite direction, not only a different value of potential often obtained as shown in Table 2 and Figs. 3, 4 and 5, but also the sign of potential is reversed sometimes as in the case of the specimen No. 14a (Fig. 5), and when we set the electrodes at another pair of cube faces, a more profound difference is found between the values of potential as shown in Table 3 and Figs. 6 and 7.

Table 2. Thermo-electric potential in the mutually opposite direction of the same specimen.

No. of specimen / Temp.	No. 13c		No. 8b		No. 14a	
	[100]	−[100]	[100]	−[100]	[100]	−[100]
	mV	mV	mV	mV	mV	mV
30°C	1.69	1.38	−0.85	−3.90	0.20	−0.77
60	2.02	3.08	−3.56	−4.88	0.85	−3.77
100	3.58	5.10	−5.01	−4.78	2.81	−5.22
120	4.95	6.27	−4.94	−4.23	4.27	−5.59
150	8.85	7.82	−3.88	−2.11	10.44	−5.37

[100] indicates that the measurement was performed in the direction of (100)→(1̄00), while −[100] shows the reverse case.

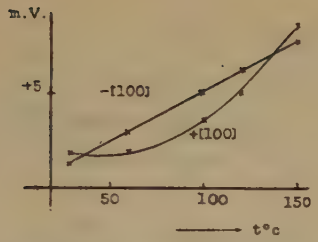

Fig. 3. The thermo-electric potential of the specimen No. 13c.

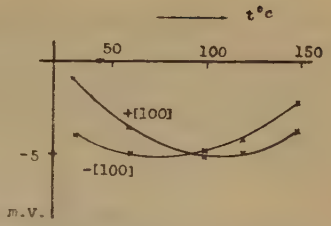

Fig. 4. The thermo-electric potential of the specimen No. 8b.

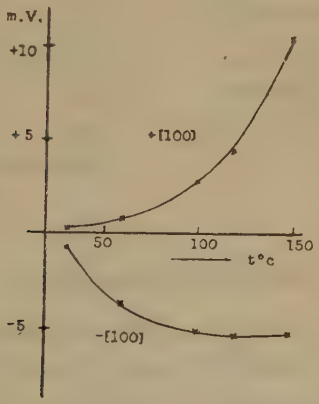

Fig. 5. The thermo-electric potential of the specimen No. 14a.

Table 3. Thermo-electric potential in the three directions each parallel to a crystallographic axis of the same specimen.

No. of specimen / Temp.	No. 4c. (Fig. 6)			No. 19a (Fig. 7)		
	[100]	[010]	[001]	[100]	[010]	[001]
	mV	mV	mV	mV	mV	mV
30°C	3.25	0.93	5.62	0.37	−0.81	3.10
60	3.76	1.25	5.03	1.09	−1.39	5.40
100	5.42	3.00	5.10	3.50	−3.25	7.44
120	6.66	4.90	5.81	5.72	−4.80	8.21
150	9.75	12.07	7.78	11.83	−8.00	8.57

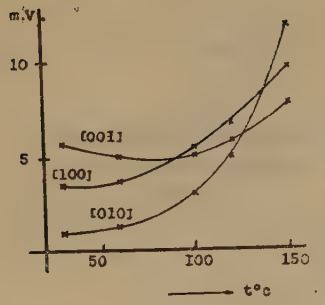

Fig. 6. The thermo-electric potential of the specimen No. 4c.

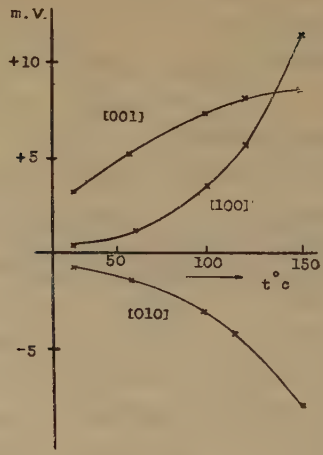

Fig. 7. The thermo-electric potential of the specimen No. 19a.

Microscopic observations

When the surface of cube face of some specimen is etched by conc. HNO_3 at 20°C., under the microscope an irregular aggregate of crystallites with a mosaic or dendritic structure appears. It seems that the thermo-electric potential of such a specimen has as a rule a positive high value as given in Table 4.

Table 4. Correlation of internal structure and thermo-electric potential.

No. of specimen	Internal structure	Thermo-electric potential. $E_{150}°$
14a	Mosaic structure	2.53 mV
17a	Mosaic structure	18.78
2a	Dendritic structure	8.69

Chemical and spectrographical analyses

Chemical analyses of thirteen specimens of the pyrite were performed following the usual methods. The results of analyses are given in the following Table 5.

Table. 5. Chemical Composition of pyrite.

Specimen No.	Fe wt%	S wt%	Insol. wt%	Total	Atomic ratio S : Fe
2a	45.39%	52.34%	1.39%	99.12%	2.01
4a	45.36	52.33	1.52	99.21	2.01
5a	45.29	51.25	2.38	99.12	1.97
6a	46.12	52.50	1.92	100.54	1.98
9a	46.32	51.85	1.71	99.88	1.95
10a	46.15	52.53	1.22	100.62	1.98
11a	46.29	52.51	1.21	100.61	1.97
12a	45.23	52.44	2.86	100.53	2.01
15a	45.20	51.73	2.23	99.16	1.99
16a	46.21	52.51	1.57	100.29	1.98
17a	46.20	51.77	1.60	99.57	1.95
19a	46.22	52.79	1.57	100.58	1.99
20a	46.18	52.68	1.03	99.89	1.98

The atomic ratio of sulfur to iron varies from 2.01 to 1.95. The specimens from No. 5 vein were also spectrographically analysed by means of Adam Hilger Spectrograph E 2. The results are tabulated as follows. (Table 6).

The authors could not find any particular relationship between the chemical composition and the thermo-electric potential.

X-ray studies

Of twenty specimens from No. 5 vein, the thermo-electric potential of which had been measured, Laue photographs perpendicular to (100) were obtained using molybdenum radiation. Among them following four types were distinguished:

Type A: All spots are distinct (Fig. 8, Plate I)

Type B: With faint diffused scattering (Fig. 9, Plate I)

Type C: With diffused scattering (Fig. 10, Plate I)

Type D: All spots have irregular-shaped figures (Fig. 11, Plate I)

Table 6. Minor elements of pyrite.

No. of specimen from No. 5 vein	Minor element*									
2a	Pb	Cu	Mn	Ag	Au	Zn	Ni	Co		
5a	Pb	Cu	Mn	Ag	Au	Co				
6a	Pb	Cu	Mn	Ag	Au	Ni	Co	Ce	Se	
7a	Pb	Cu	Mn	Ag	Cs	Co	Cr			
8a	Pb	Cu	Mn	Ag	Au	Co	Se	Cr		
9a	Pb	Cu	Mn	Au	V					
10a	Cu	Mn	Au	Ba	V					
13a	Pb	Cu	Mn	Au	Ba	Zn	V	Cr	Ni	Co
18a	Pb	Cu	Mn	Ag	Zn					
20a	Pb	Cu	Mn	Ag	Au	Zn				

* All specimens contain Fe, Si, Mg, Ti and Al.

X-ray powder patterns of the type specimen of each type were studied by means of a Norelco Spectrometer. No conspicuous difference was found in the lattice constants of the specimens.

As for the specimens which show mosaic structures after etching, Laue photographs perpendicular to (100) were taken also at every successive location 1 mm. apart from each other on (100). The photographs as shown in Figs. 12~16, Plate II indicate that the specimen, which is apparently homogeneous, is made up of slightly dislocated blocks.

In general thermo-electric potentials of specimen of type A have negative or positive low value, while those of the specimens which give rise to diffused scattering on Laue spots or mosaic structure after etching have positive high values. In Table 7 examples of

each type are shown, indicating the relation between the types of Laue spots and the thermo-electric potentials of pyrite.

Table 7. Type of Laue photographs and thermo-electric potentials of the type specimens.

No. of specimen from No. 5 vein	Type of Laue diffraction pattern	Thermo-electric potential. E_{150}°
11a	Type A	0.82 mV
17a	Type B	18.78
15a	Type C	12.05
3a	Type D	12.37

Summary

A wide variation of the thermo-electric potentials, ranging from 19.82 mV. to −12.32 mV., are observed on pyrite from the Tutiya Isizaki mine, Hokkaidô. The specimens associated with copper ores show negative potential.

From X-ray diffraction studies, it is evident that the potentials of nearly perfect crystals have positive low or negative values, while those of crystals with structural irregularities have positive high values.

The atomic ratio of sulfur to iron varies from 2.01 to 1.95, and it seems that there is no decisive effect of chemical composition upon variation of thermo-electric properties.

As might be expected it is concluded that structural irregularities may have more influence upon the thermo-electric properties of pyrite than any other factors.

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Fig. 8

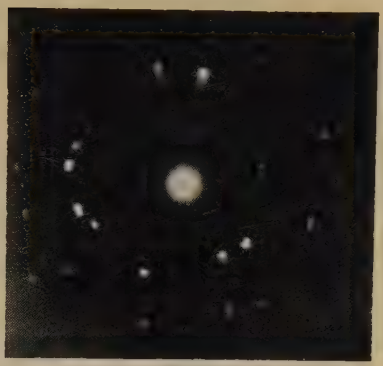

Fig. 10

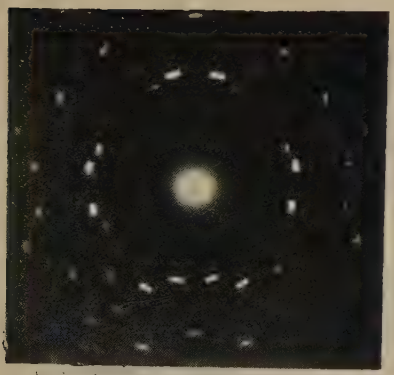

Fig. 9

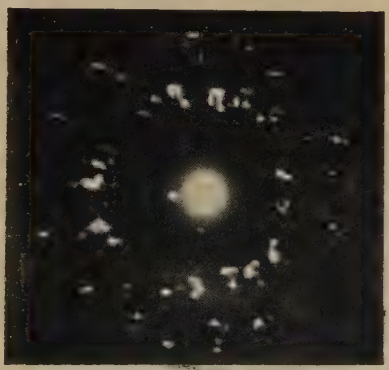

Fig. 11

Fig. 8. Laue spots of Type A, showing distinctive shape of reflection. Incident radiation normal to (100).
Fig. 9. Laue spots of Type B, showing faint diffuse scattering. ditto.
Fig. 10. Laue spots of Type C, showing diffuse scattering. ditto.
Fig. 11. Laue spots of Type D, showing irregular-shaped figures. ditto.

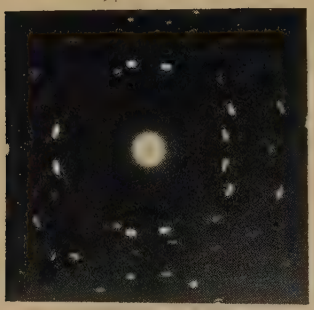

Fig. 12

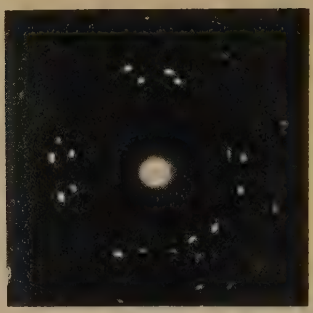

Fig. 15

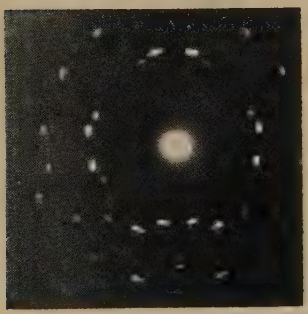

Fig. 13

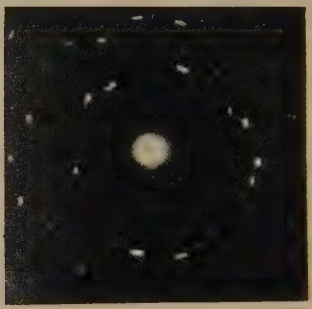

Fig. 16

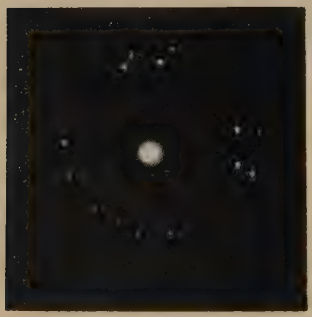

Fig. 14

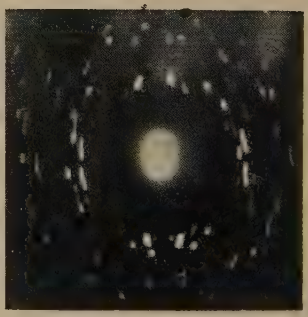

Fig. 17

Figs. 12-16. A series of Laue photographs of pyrite with X-ray beam normal to (100) at every successive location 1 mm. apart from each other along [010] on (100).

Fig. 17. A Laue photograph of the same specimen with X-ray beam perpendicular to (100) by a long slit method of Yoshida and Tanaka.

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ON THE DIADOCHIC SUBSTITUTION IN SILICATES*

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ABSTRACT

The diadochic substitution of elements in the structure of silicate minerals is primarily controlled by the potential energies arising from the linkage of vicarious cations with an oxygen anion. A quantity, the index of diadochy, is proposed as a measure for the contribution of a cation to the potential energy, and is calculated for a number of elements of geological significance. The indices of diadochy of the elements harmonize generally with the natural geochemical behavior of the elements. Furthermore, possible effects of controlling factors other than the index of diadochy on the substitution are considered.

Introduction

Some atoms or ions are capable of replacing one another at a certain lattice site in a mineral. V.M. Goldschmidt[4) 5) 6)] states that the substitution takes place either by camouflage, capture or admission depending on electrostatic charges and radii of the elements concerned. He also points out that two elements which constitute a substituting pair have similar ionization potentials, together with the same electrostatic charge and closely similar radii.

These principles are known as the Goldschmidt rule, and the veracity of the rule is supported by numerous mineralogical and geochemical data.[10) 11) 25) 26) 29)] In some cases, however, the rule is at variance with geochemical observations. Radii of the interchangeable atoms or ions are not always similar, and the distribution of

* Read at the Annual Meeting of the Mineralogical Society of Japan held in Tokyo on June 5, 1953.

element in minerals cannot be explained from size relation alone.[27] On the other hand, despite a rather appreciable difference in the ionization potentials, two elements, such as rubidium and thallium, having the same electrostatic charge and the same radius, are known to behave similarly in rocks.[1,24] Thus the substitution is not satisfactorily explained by considering separately any one of the controlling factors. It is rather necessary to consider the combined effect of the different factors. The present study is a step towards such an intention.

Theoretical considerations

The diadochic substitution between two elements in a mineral takes place in such a way that the change of the free energy of the mineral which arises from the substitution remains minimum so long as the mineral crystallizes in an equilibrium condition. Therefore, if we know the free energy of a given mineral under an arbitrary condition, we are able to predict, a priori, among which elements the substitution takes place actually in the structure of the mineral in question.

According to statistical mechanics, the free energy of a system is derived from the partition function for the system. For the sake of simplicity, let us assume that the system is not affected by any external force. In such a case, disregarding the zero-point energy, the energy of the system that is an integrant in the partition function is written as a sum of the kinetic energies of atoms or ions constituting the system and the potential energies arising from the linkage of them. After the classical theory,* the partition function Z is given by

$$Z=\frac{1}{h^{3N}}\int\cdots\cdots\int\exp\left\{-(E+V)/kT\right\}dp_1\cdots\cdots dp_N,\ dq_1\cdots\cdots dq_N, \qquad (1)$$

* See, for example, J. C. Slater: Introduction to Chemical Physics, Chap. III, McGraw-Hill Book Co., Inc., 1st ed., 1939.

where N is the number of the atoms or ions constituting the system; E and V are the kinetic energy and the potential energy, respectively. q_i is the space coordinate of the ith atom or ion in the system, p_i the conjugate momentum, and dp_1 represents dp_{1x}, dp_{1y}, and dp_{1z}, and so on. The factor h^{3N} is introduced so that Z may be a nondimensional quantity. Then the Helmholtz free energy is written as follows:

$$F=-kT\log Z \qquad (2)$$

Thus, if the kinetic energy and the potential energy are known as the function of coordinates and momenta, the equations (1) and (2) give a perfectly direct and straightforward way of deriving the Helmholtz free energy of the system.

Unfortunately, we are unable to carry out analytically the integration of the equation (1) for such a complex system as silicate mineral. Therefore, we cannot obtain any fundamental theory on the diadochic substitution. Then, for the present study, the problem will be considered with some approximations.

According to equations (1) and (2), it may be assumed that the Helmholtz free energy is controlled by the potential energy to a considerable extent, especially at low temperature, and that the diadochic substitution is primarily controlled by the potential energy. In case where the system is not affected by any external force, the potential energy of a crystal is given by the potential of interaction between two atoms or ions in the crystal. The atoms or ions of the interchangeable elements are linked to oxygen atoms or ions. Let us assume then that the bond is exclusively of ionic character, and also that the potential energy arises from two forces, namely the electrostatic force due to the Coulomb interaction between the charged ions, and the repulsive force between the ions, resulting from the exclusion principle. Then the bond energy Φ between oxygen anions and interchangeable cations is

$$\Phi = -\frac{NAe^2 Z_O Z_M}{R}\left(1-\frac{1}{n}\right), \qquad (3)$$

where N is the total number of the anions and cations in a crystal, and A the Madelung constant. e is the unit charge per electron; Z_O and Z_M represent the electrovalencies of the oxygen anion and the interchangeable cation respectively. R is the spacing between the nearest neighbors of the anions and cations at equilibrium positions; and n is the Born exponent of repulsion.

For the present purpose, it is not necessary to calculate the numerical value of the bond energy, because it may be assumed that the change in the free energy of the crystal caused by the substitution depends on the dissimilarity of the degree of contribution of the vicarious cations to the bond energy. The degree of contribution of each cation may be measured by dividing the terms related to the cation in the equation (3) by its coordination number.

The coordination number of any cation in silicate minerals is inferred from the ratio of its radius to that of the oxygen anion.[20] As a matter of fact, however, it is also possible for a cation to have a coodination number other than that inferred by the simple geometrical method, for any ion is not strictly a rigid body. E. F. Osborn[17] suggested that the coordination number of a cation is variable, depending on the type and concentration of the other ions present in the same structure, temperature, and pressure. For instance, the coordination number of K^+ may vary from 6 to 12, and Si^{4+} is found to have even a coordination number of 6 in the artificial SiP_2O_7, though it has the coordination number of 4 in all known silicates. However, as suggested by F. E. Wickman,[30] cations are not equally stable in various coordinations allowed for them. The fact that Si^{4+} has a coordination number of 4 in all the natural minerals strongly indicates its higher stability in 4-fold coordination than in 6-fold one under a condition prevailing in nature. It may be assumed then that any cation is unable to have a coordination

number other than that inferred from its ionic size without increasing the free energy of the crystal in which it exists.

Thus, regarding N and A in the equation (3) as an invariable so long as the substitution occurs in a given structure, the following gives a measure for the contribution of the interchangeable cation to the bond energy of the crystal:

$$D=\frac{Z_M}{CR}\left(1-\frac{1}{n}\right), \qquad (4)$$

where C is the presumed coordination number of the cation.

R is approximately obtained by the sum of ionic radii of the two ions, and n is denoted by the average of n for oxygen and that for the cation. Therefore, regarding the ionic radius and the exponent of repulsion of oxygen anion as constant, D depends on the electrovalency, ionic radius, and the electronic configuration of the cation alone, and hence is characteristic of the cation. D is called here the "index of diadochy" of cation. Then the change of the free energy of a crystal caused by the substitution is primarily measured by the difference in the indices of diadochy of the vicarious cations. If the substitution takes place between two elements differing markedly in the indices from each other, the change of the free energy of the crystal is greater than that required by the change of the physico-chemical condition which caused the substitution. It follows then that the indices of diadochy of the cations which are mutually replaceable should be close together.

The diadochism is therefore to be expected to take place between those two elements which have the same electrovalency, similar ionic radii and similar chemical characters. Even though two cations have different electrovalencies, however, they may be capable of mutually replacing if only their ionic radii are dissimilar in such a manner as compensating the difference in the electrovalencies, resulting in a similarity of the indices of diadochy.

The requirement of the similarity of the ionization potentials of

the vicarious cations is not directly deduced from the equation (4), because the equation holds for purely ionic crystals. The reason why the similarity of the ionization potentials is required is as follow: The nature of the chemical bond depends on the electronegativities of the elements concerned.[20] The greater is the electronegativity of the element linked to oxygen, the less is the tendency for the ionic character of the bond. As regards monovalent atoms, the electronegativity is, in turn, measured by the average of the ionization energy and the electron affinity of the atom.[16] [17] For multivalent atoms corrections must be made owing to the different state of the atoms and ions, but the situation is the same. Accordingly, the ionization potential may be regarded as a factor which determines the nature of the chemical bond. Then, if two elements have the same electrovalency and ionic radius but different ionization potentials, they are unable to replace one another without reducing the stability of the crystal concerned. In such a case, the greater is the difference between the ionization potentials of the elements, the more is the difficulty of their diadochism. On the other hand, even if two cations have somewhat dissimilar ionization potentials, they may substitute for each other in the case where the difference in the ionization potentials has merely a negligible influence on the cohesive energy of the crystal, as referred later.

Indices of diadochy of cations

The indices of diadochy are computed for the elements of geological significance. The ionic radii for 6-fold coordination are taken from the Ahrens table[2] from which the univalent radii are derived. The probable coordination number of each cations is determined by the ratio of its univalent radius to the univalent radius of the oxygen anion (Table 1). R is given by the sum of the ionic radii of the oxygen anion and that of each cation for presumed coordination. Values of n for various types of ion are given in Table 2. n

in the equation (4) is denoted by the average of n for oxygen and that for the cation concerned.

Table 3 gives the indices of diadochy of cations, together with the values mentioned above.

Table 1. Values of the minimum radius ratio for stability of various coordination polyhedra (after Pauling[20]).

Polyhedron	Coordination	Minimum radius ratio
Cubo-octahedron	12	1.000
	9	0.732
Cube	8	.732
Square antiprism	8	.645
	7	.592
Octahedron	6	.414
Tetrahedron	4	.225

Table 2. n for various types of ion (after Pauling[19]).

Types of ion	n
He	5
Ne	7
A, Cu^+	9
Kr, Ag^+	10
Xe, Au^+	12

Table 3. The indices of diadochy of cations.

Ions	R_z (6)*)	R_1**)	R_1/R_{O1}	C	R_z (C)***)	n	Index of diadochy D
P^{5+}	0.35	0.60	0.34	4	0.33	7	0.62
As^{5+}	0.46	0.53	0.30	4	0.44	9	0.60
Si^{4+}	0.42	0.67	0.38	4	0.39	7	0.48
Ge^{4+}	0.53	0.75	0.43	4	0.50	9	0.46
B^{3+}	0.23	0.40	0.23	4	0.21	5	0.39
Bi^{5+}	0.74	0.99	0.56	6	0.74	12	0.35
Al^{3+}	0.51	0.73	0.41	4	0.47	7	0.35
				6	0.51	7	0.23
Ti^{4+}	0.68	0.96	0.55	6	0.68	9	0.28
Mo^{4+}	0.70	0.95	0.54	6	0.70	10	0.28
W^{4+}	0.70	0.90	0.51	6	0.70	12	0.28
Nb^{4+}	0.74	1.01	0.57	6	0.74	10	0.28
Hf^{4+}	0.78	1.01	0.57	6	0.78	12	0.27
Be^{2+}	0.35	0.49	0.28	4	0.32	5	0.24
Ga^{3+}	0.62	0.81	0.46	6	0.62	9	0.22
Co^{3+}	0.63	0.83	0.47	6	0 63	9	0.22
Cr^{3+}	0.63	0.83	0.47	6	0.63	9	0.22
Fe^{3+}	0.64	0.84	0.48	6	0.64	9	0.22
Mn^{3+}	0.66	0.87	0.49	6	0.66	9	0.21
V^{3+}	0.74	0.98	0.56	6	0.74	9	0.21
In^{3+}	0.81	1.04	0.59	6	0.81	10	0.20
Sc^{3+}	0.81	1.04	0.59	6	0.81	9	0.20
Zr^{4+}	0.79	1.07	0.61	8	0.81	10	0.20
U^{4+}	0.97	1.25	0.71	8	1.00	12	0.19
Th^{4+}	1.02	1.32	0.75	9	1.06	12	0.16
Mg^{2+}	0.66	0.83	0.47	6	0.66	7	0.14
Ni^{2+}	0.69	0.82	0.47	6	0.69	9	0.14
Sn^{2+}	0.71	0.83	0.47	6	0.71	10	0.14
Co^{2+}	0.72	0.86	0.49	6	0.72	9	0.14
Cu^{2+}	0.72	0.86	0.49	6	0.72	9	0.14
Fe^{2+}	0.74	0.88	0.50	6	0.74	9	0.14
Zn^{2+}	0.74	0.88	0.50	6	0.74	9	0.14
Y^{3+}	0.92	1.18	0.67	8	0.95	10	0.14
Mn^{2+}	0.80	0.95	0.54	6	0.80	9	0.13

Table 3—*Continued*

La^{3+}	1.14	1.39	0.79	9	1.19	12	0.12
Li^{+}	0.68	0.68	0.39	4	0.61	5	0.10
Cd^{2+}	0.97	1.14	0.65	8	1.00	10	0.09
Ca^{2+}	0.99	1.18	0.67	8	1.03	9	0.09
Sr^{2+}	1.12	1.31	0.74	9	1.17	10	0.08
Pb^{2+}	1.20	1.36	0.77	9	1.25	12	0.08
Ba^{2+}	1.34	1.51	0.86	9	1.39	12	0.07
Cu^{+}	0.96	0.96	0.55	6	0.96	9	0.06
Na^{+}	0.97	0.97	0.55	6	0.97	7	0.06
Ag^{+}	1.26	1.26	0.72	8	1.30	10	0.04
K^{+}	1.33	1.33	0.75	9	1.40	9	0.03
Tl^{+}	1.47	1.47	0.84	9	1.53	12	0.03
Rb^{+}	1.47	1.47	0.84	9	1.54	10	0.03
Cs^{+}	1.67	1.67	0.95	12	1.79	12	0.02

*) The ionic radii for 6 fold coordination (after Ahrens[2])

**) The univalent radii calculated from the equation: $R_1 = R_z Z^{\frac{2}{n-1}}$

***) The ionic radii for presumed coordination calculated from the equation: $R(C) = R(6) \cdot \left\{\frac{C}{6}\right\}^{\frac{1}{n-1}}$

Discussion

According to the previous considerations, if the diadochic substitution does take place in an equilibrium condition, the vicarious cations should have similar indices of diadochy. The smaller is the difference between the indices of the two cations, the more easily they can substitute for each other. Then, after the equation (4), it is favorable for two cations to have the same electrovalency, similar ionic radii and similar electronic configurations in order to substitute for each other.

Table 3 shows that some cations have the same index of diadochy. There are several pairs of such cations, for example, Fe^{3+}—Cr^{3+}, Fe^{2+}—Mg^{2+}, Ca^{2+}—Cd^{2+}, and Rb^{+}—Tl^{+}. It is well known that the diadochy of the cations of each pair takes place quite commonly in silicate minerals. Then the two cations may be ragarded

as being vicarious due to the identity of elecrovalencies and the similarity of ionic radii and chemical characters, and thus to the resultant identity of the indices of diadochy.

However, a rather appreciable difference in either electrovalencies or ionic radii of two cations does not necessarily make the substitution difficult for the cations if only the combined effect of the factors on the indices of each cation is similar to each other.

The ionic radius of U^{4+} differs remarkably from that of Zr^{4+}. Owing to the similarity of the indices of diadochy, however, they may be vicarious for each other, as assumed in the structure of zircon. A similar relation exists between Th^{4+} and Zr^{4+}.

Ge^{4+} has the same electrovalency as Si^{4+}, and a closer ionic radius to that of Al^{3+} than to Si^{4+}. The close geochemical association of germanium with silicon but not with aluminum is explained by the fact that the index of diadochy of Ge^{4+} (0.46)*) is much more similar to that of Si^{4+} (0.48) than to Al^{3+} (0.35).

On the other hand, La^{3+} (0.12) probably replaces some divalent cations, such as Mg^{2+} (0.14), Fe^{2+} (0.14) or Ca^{2+} (0.09), instead of trivalent Al^{3+} (0.23) or Fe^{3+} (0.22).

H.W. Jaffe[12] showed that yttrium is found in some garnets rich in manganese and ferrous iron and poor in magnesium, calcium and ferric iron, and suggested that Y^{3+} occupies Mn^{2+} positions in the garnet lattice. This is in accord with the Goldschmidt rule which permits the difference of the ionic radius up to 15 per cent for the substitution to take place. However, the fact found by Jaffe may be better explained as due to the similarity of the index of diadochy of Y^{3+} (0.14) to that of Mn^{2+} (0.13) rather than to that of Ca^{2+} (0.09). In ionic radius Y^{3+} is closer to Ca^{2+} than to Mn^{2+}.

Thus the indices of diadochy of cations harmonize generally with the natural geochemical behavior of the cations. Yet the other physical and chemical factors than the index should be taken into

* In the following, figure in parenthesis refers to the index of diadochy of the cation concerned except where otherwise specified.

consideration for better explanations of the problem of substitution, for the factors are entirely disregarded in deriving the index because of the difficulty in quantitative treatments. In the following, let us empirically consider some probable effects of these factors on the substitution.

1) It cannot be shown quantitatively how much difference in the indices of diadochy is permitted for the cations to replace each other. The maximum difference may change with the type of structure and, even in a given structure, at lattice points which are structurally not equivalent. This is partly ascribed to the method used for calculating the index of diadochy. That is, as the coordination number of each cation, we used a figure obtained by a simple geometrical way, and we also assumed that the Madelung constant is unchangeable in any types of substitution.

2) Temperature has also an important bearing upon the maximum difference, as seen from the equations (1) and (2). At elevated temperature, the proportion of the kinetic energy in the free energy of a crystal is greater than at lower temperature, so that an appreciable difference in the indices of diadochy of the cations may have little effect on the free energy of the crystal. It follows that the difference in the indices of diadochy permitted for cations to substitute for each other may be greater at higher temperatures than at lower temperatures.

H. S. Yoder and M. L. Keith[31] has experimentally demonstrated that silicon is completely replaced by aluminum in the artificial garnet, yttroalumite, crystallized at 1970°C. H. Kuno[14] revealed by the study on the ion substitution in clinopyroxenes that in some of them from volcanic rocks formed at high temperature Si^{4+} is replaced not only by Al^{3+}, but also by Ti^{4+} and/or Fe^{3+}. While in the clinopyroxenes from plutonic rocks and metamorphic rocks Si^{4+} is considered as being replacable by neither Ti^{4+} nor Fe^{3+} (Hess[9]).

Furthermore, in a given crystal, the tolerance in relation to the indices of the vicarious cations would be greater for the substitution

at the lattice site which is considered as being fixed at higher temperatures. In pyroxene, for example, a part of Si^{4+} (0.48) is nearly always replaced by Al^{3+} (0.35), while Ca^{2+} (0.09) is hardly replaced by K^{+}(0.03).

3) The degree of substitution of a pair of cations having a given difference in their indices of diadochy depends on temperature.

As posturated by H. H. Hess[8] and demonstrated experimentally by L. Atlas,[3] Ca is more soluble in orthopyroxenes at higher temperatures than at lower temperatures. H. Kuno[13] ascertained the relation by the systematic study on orthopyroxenes from volcanic rocks.

Thus the substitution Mg^{2+} —Ca^{2+}, and Fe^{2+} —Ca^{2+} prevails at considerably high temperatures, though the indices of diadochy of the two cations in each pair are rather dissimilar. At lower temperatures, however, the two cations substitute for each other to a more limited extent. This results in the formation of the exolusion lamellae found in some pyroxenes. It is the case with the substitution Ca^{2+} —Na^{+}, and Na^{+}—K^{+} in feldspars.

From the same reason, some minerals occurring in metamorphic rocks show more limited miscibility than that shown by the same minerals in igneous rocks.

4) In the preceding discussions, the effect of pressure was entirely disregarded, and the Helmholtz free energy was considered as a clue to the substitution. However, the partition function really depends not only on temperature but also on pressure, and hence the diadochism in natural minerals should be discussed on the basis of the Gibbs free energy, instead of the Helmholtz free energy. Although the quantitative treatment of the effect of pressure on the diadochism is very difficult at present, it is possibly said that the pressure appears to change the stable coordination number of a cation.

It has been shown by F. E. Wickman[30] and J. B. Thompson[28] that, if the temperature remains constant, Al^{3+} prefers to enter the

tetrahedral position at lower pressures, while it prefers to enter the octahedral position at higher pressures. Consequently, Al^{3+} has a smaller index of diadochy (0.23) at a higher pressure. Provided that the other conditions are the same, it is probably difficult for Al^{3+} to replace Si^{4+} at higher pressures.

5) It is not only the Coulomb force and the repulsive force that controls the cohesive energy of a crystal, as previously assumed. Besides them, the van der Waals attractive force and the zero-point energy affect the cohesive energy.

F. London[15] showed that the dipole moment of an atom due to the instantaneous configuration of electrons and nucleus of the atom causes the polarization of the adjacent atoms, resulting in an attractive force which contributes greatly to the van der Waals attraction. The van der Waals potential U between any pair of atoms or ions can be conveniently given by*)

$$U=-\frac{3}{2}\frac{1}{(4\pi\epsilon_0)^2 R^6}\frac{\Delta E_1\cdot\Delta E_2}{\Delta E_1+\Delta E_2}\alpha_1\cdot\alpha_2,$$

where ϵ_0 is the permittivity of free space, R the distance between the two atoms, ΔE the energy difference between the ground state and the principal excited state, and α the polarizability in the electrostatic field. Subscripts 1 and 2 refer to each of the two atoms respectively. ΔE can be estimated from the series limit frequency of the discrete spectrum of each atom, and generally has a value close to that of the energy of ionization.

This term actually is the first term in an infinite series of terms that successively decrease in importance. The next term, which is ascribed to the dipole-quadrupole interaction, varies with the inverse eighth power of the distance and usually is about one-tenth of the former term at the observed interionic distance.

The zero-point energy has also some influence on the cohesive

* See, for example, John C. Slater: Quantum Theory of Matter, Chap. 13, McGraw-Hill Book Co., Inc., 1st ed., 1951.

energy, though it does not arise from the interaction between the charged ions. It is proportional to the Debye temperature of the atoms concerned.

Even though the van der Waals attraction and the zero-point energy do not appreciablly affect the cohesive energy as a whole, they may play a considerably important role in determining the relative stability of two different crystals. Unfortunately, however, we have little data to calculate these terms at present. Yet it may be said that two atoms having markedly different Debye temperatures, ionization energies and, especially, polarizabilities can hardly substitute for each other even if they have closely similar indices of diadochy. It is especially so in the case of ions of smaller sizes. In the case of ions of considerably large size, such as rubidium and thallium, a rather appreciable difference in the ionization potentials would have little influence on the diadochism if their polarizabilities are closely similar.

6) The substitution is also controlled by the nature of bond between the oxygen and the interchangeable element (Fyfe[4]; Ramberg[22]). The assumption of purely ionic character of the bond is far from the case for some elements.

According to Pauling[20] the amount of ionic character of a bond between two elements, electronegativities of which are x_A and x_B respectively, is given by

$$\text{Amount of ionic character} = 1 - e^{-c(x_A - x_B)^2},$$

in which c has the value $\frac{1}{4}$. Thus B-O bond is about 40% ionic, namely the covalent character predominates in the bond, and Cs-O bond is approximately 90% ionic, that is, the bond is essentially ionic with but limited covalent character. These are extreme examples, and the bonds between the oxygen and the other elements listed in Table 3 show ionic tendency ranging between these two extremities.

Since such a bond is interpreted as resonating between the purely ionic state and the purely covalent state, its energy is somewhat greater than that estimated on the basis of the assumption of purely ionic character of the bond. Then the contribution of the interchangeable element to the bond energy may also differ from that given by the equation (4) and shown in Table 3. The difference depends both on energies of the two resonating structures and on resonance energy which is determined by the amount of interaction of the two structures (Pauling and Wilson[21]).

With regard to most of bonds in question, these quantities are not still obtained by theoretical calculations, nor by experimental data. At least, however, it is suitable for elements to have closely similar electronegativities in order to replace each other.

7) The effective electronegativity of oxygen should also be considered. In silicate minerals the cations are actually linked not with the free oxygen anion but with the complex Si-O anion. H. Ramberg[22) 23)] has shown that the electronegativity of oxygen in silicates increases stepwise with the sequence, orthosilicate—metasilicate—phyllosilicate—tectosilicate. Therefore the index of diadochy of a cation may change with the type of structure. In this connection, it should be recalled that in deriving the index of diadochy the Madelung constant is assumed to be invariable and disregarded. It follows then that the index of diadochy may serve as a basis for the discussion of the problem of substitution in a given type of structure but not for the discussion of the problem of the distribution of cations in coexisting minerals.

Conclusions

The index of diadochy of a cation is a measure for the contribution of a cation to the cohesive energy of the crystal which containes the cation. It depends on electrovalency, ionic radius, coordination number, and the exponent of repulsion of the cation, and

hence is characteristic of each cation. The diadochy is primarily controlled by the indices of the cations substituting for each other.

From theoretical considerations as well as geochemical observations, it may be concluded that the vicarious cations advantageously have similar indices of diacochy. However, since the indices of diadochy are calculated with some approximations, they are far from satisfactory as a criterion with which we can discuss the substitution phenomena.

The influence of the other factors on the substitution, such as temperature and pressure as well as polarizability, ionization potential and electronegativity of element, is the subjct of a further study.

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SHORT COMMUNICATIONS

RECUEIL MINERALOGIQUE (II)

JUN ITO

l'Institut de Minéralogie, Université de Tokyo.

(3) *Andalousite de Koshinmen*

L'andalousite de Koshinmen* prés de Wiiu,** Corée du Nord a été decouverte par M. Takahashi,[1] dans le schiste cristallin du Précambrien qui s'étend en grande partie dans cette région. On y trouve ça et là les veines formés des cristaux de l'andalousite large de 5cm. à 30cm. environ qui passent parallelement à la direction de la schisteusité dominante. L'auteur doit l'échantillon à M. T. Katano. Il est un groupement des cristaux réunis quasi-parallelement à (001) et couvert par le sillimanite produit de l'altération de l'andalousite. Les autres mineraux associés sont le quartz, le muscovite, le biotite et le sericite. Aucune face n'est observé que m(110).

Quand on coupe cet échantillon perpendiculaire à (001), on peut observer les deux parties du cristal différenment colorées, une étant rouge autre blanche. L'auteur a séparé ces deux parties de l'andalousite qui s'unient étroitement l'un et l'autre et a tenté leure analyse chimique aussi que celle du sillimanite. L'examen optique, fait aussi par l'auteur au moyen de la réfractomètre Pulfrich a servi à établir les différences des deux parties de l'andalousite comme il suit.

---

* 古津面　　** 義州

Table 2. Les compositions chimiques et les constants optiques.

	Andalousite rouge	Andalousite blanche	Sillimanite
SiO_2	36.36%	36.28%	36.66%
Al_2O_3	61.23	61.14	59.42
Fe_2O_3	1.46	1.04	0.78
MnO	0.00	0.05	0.00
MgO, CaO	0.16	0.27	0.23
Na_2O	0.04	0.11	n.d.
H_2O	0.47	0.68	3.16
Total	99.72%	99.57%	100.25%
n_p	1.637	1.632	
n_m	1.644	1.638	
n_g	1.650	1.646	
$n_g - n_p$	0.013	0.014	
2V(−)	73°±2	80°±2	

Les formules moléculares sont suivantes.

L'andalousite blanche $Al_{1.98}\ Fe_{0.03}\ Si_{1.00}\ O_{5.00}$

„ rouge $Al_{1.98}\ Fe_{0.02}\ Si_{1.00}\ O_{5.00}$

Par suites des donnés ci-dessus on pourrait apercevoir les faits suivants. La partie rouge de l'andalousite est plus ferrugineuse que la partie blanche mais au propos des indices de réfractions, celles de la partie rouge sont plus hautes que celles de la blanche, mais au contraire 2V de celle-là est moin grand que celle-ci.

Veuillez me permettre de faire remerciement à M. le docteur A. Miyashiro, l'Institut de Géologie, qui m'a donné plusieur repris des conseils.

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